NBS TECHNICAL NOTE 828

Measures for Air Quality (1972-1973)

Annual Report—FY 1973

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

JUN 25 1974

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Part of the Center for Radiation Research.
[3] Located at Boulder, Colorado 80302.
[4] Part of the Center for Building Technology.

Measures for Air Quality (1972-1973)

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James R. McNesby

Institute for Materials Research
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Washington, D.C. 20234

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NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, *Director*

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Assistant Secretary of Commerce for Science and Technology, Dr. Betsy Ancker-Johnson examines the first commercial prototype of the NBS fluorescence monitor for SO_2. Looking on are from left Dr. Ray Chuan, Celesco Industries, Inc., Dr. R. G. Vande Vrede, President, Celesco Industries, Inc., Dr. Hideo Okabe, the NBS inventor and NBS Director, Dr. Richard W. Roberts.

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MEASURES FOR AIR QUALITY (1972-1973)

ANNUAL REPORT-FY 1973

James R. McNesby

This report is a project-by-project description of the Measures for Air Quality program covering the fiscal years 1972 and 1973. Participation in the program is bureau-wide but the program office operates out of the Institute for Materials Research. Although air pollution measurement science has formed the major thrust of the program, it has been extended in FY 73 to include the beginnings of a water pollution effort to respond to new needs, particularly those arising out of the requirements of the Federal Water Pollution Control Act of 1972. A report on the MAQ program for FY 72 was not issued. However, the project reports in the current document include progress made during FY 72 for those FY 73 projects which were active in FY 72. Where a project was terminated at the end of FY 72 its description is included in the present document with appropriate notation.

In water pollution the situation is much more complex since there are many more pollutants in more types of water that will be subject to control under the Federal Water Pollution Control Act of 1972. When a pollutant is of concern in the discharge permit program, water quality standards, the toxic pollutant list and in the specimen bank program, the state of the measurement art is scrutinized at NBS and the need for development assessed.

Key words: Air pollution; measurement; Standard Reference Material; water pollution.

Although a report on the MAQ program for FY 72 was not issued, the project reports in the current document include progress made during FY 72 for those FY 73 projects which were active in FY 72. Where a project was terminated at the end of FY 72 its description is included in the present document with appropriate notation.

The following projects begun in FY 71 (NBS Technical Note 711) were terminated at the end of that fiscal year: IDENTIFICATION AND STUDY OF CRYSTALLINE COMPONENTS OF PARTICULATE MATTER IN AIR POLLUTION SAMPLES -- This project stimulated the interest of the National Institute of Occupational Safety and Health in analysis of quartz in industrial atmospheres and forms the basis of a project reported in the current document. INDOOR AIR POLLUTION -- The continuation of this project was judged not to be of a high priority. MOLECULAR COMPLEXES OF GASEOUS POLLUTANTS -- The early results failed to turn up sufficiently promising systems for continued study. FRICTIONAL DEGRADATION OF RUBBER -- The project, completed in FY 72, was a joint project with EPA. MODULATED INFRARED LASER ABSORPTION TECHNIQUES FOR ATMOSPHERIC POLLUTANT MEASUREMENTS -- This project was judged not to be of sufficiently high priority to carry into the experimental phase. ATOMIC EMISSION DETECTOR -- The project was completed. THE ROLE OF THE LOWEST EXCITED METASTABLE STATE OF SO_2 IN THE PHOTOCHEMICAL PRODUCTION OF AIR POLLUTANTS The report was terminated because of the departure of a guest worker. Several "Minor" MAQ projects described in NBS Technical Note 711 were dropped for various reasons. Those "Minor" MAQ projects continued included Calibration Standards Via Purolysis,

Fluorescence Detector for SO_2, Nitric Oxide SRM Development. Fiscal Year 1971 projects supported by the Environmental Protection Agency and completed in FY 71 included Instrumentation Assistance to the National Air Pollution Control Administration and Emissions of Rubber from Auto Tires.

The National Bureau of Standards has given its primary attention to needs for new measurement techniques and Standard Reference Materials for the six "Criteria Pollutants" (SO_2, NO_x, CO, Hydrocarbons, O_3 and particulate matter) in three media---ambient air, stack gases and auto exhaust. The matrix is shown in Figure 1. To find the description of a project impacting on a particular matrix element, locate the matrix element in Figure 1 and read off the number of the project whose title is listed in the table of contents.

The Measures for Air Quality program was extended in FY 73 to include the beginnings of a water pollution program to respond to new measurements needs, particularly those arising out of the requirements of the Federal Water Pollution Control Act of 1972. In water pollution the situation is much more complex than in air since there are many more pollutants in more types of water that will be subject to control under the Federal Water Pollution Control Act of 1972. Pollutant discharges are limited for 71 parameters (FR 38, No. 199, Page 28757) and EPA has in draft form restrictions on 162 contaminants in receiving water including 97 pesticides. Because it is impossible for NBS to give attention to all of these pollutants, we must consider other criteria for ordering priorities. For compliance with section 307 of the Federal Water Pollution Control Act, the EPA presented a list of 9 "Toxic Pollutants" emitted from point sources and known to be

AIR POLLUTION PROJECTS[a]

	AMBIENT		STACK		AUTO	
	Measure-ment	SRM	Measure-ment	SRM	Measure-ment	SRM
SO_2	2,3,17	1,20,21	3	17,20	b	20
NO_x	3,4,8,17,26,27	1,7,20	3,4,8	5,6,17,20	3,4,8,22	3,5,6,20
Particulates	9,10,12,13,14	11,12,16,17,18	9,10,23	11	9,10	b
CO	24	5	b	5[b]	22	5
Hydrocarbons	d	19,20	b	5,19,20[b]	22	5,19,20
Oxidants (O_3)	d	e	b	b	b	b
Other pollutants	24,26,27	17,18,20	b	20[c]	b	20[c]

[a]The entries correspond to the numbers of the projects listed in the Table of Contents.

[b]No national standard is applicable.

[c]This project anticipates that needs will arise even though no national standard is applicable.

[d]Entries are absent because of the existence of reasonably good measurement technology.

[e]NBS has developed for EPA (in FY 71) an ozone generator and expects to continue the project in FY 74.

FIGURE 1

damaging to the public health. In this list appear the metals mercury and cadmium. Also, the Human Studies Laboratory of EPA has named mercury, cadmium, lead, arsenic, zinc, copper, nickel, vanadium, selenium, berylium, chromium, and manganese as first priority elements in their projected National Environmental Specimen Bank. When a pollutant is of concern in the discharge permit program, water quality standards, the toxic pollutant list and in the specimen bank program, the state of the measurement art is scrutinized at NBS. Among the metals, mercury and cadmium appear to be of most interest. It is to be noted that analytical methods are specified usually from one or more of three sources, 1,2,3.

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1. Standard Methods for the Examination of Water and Waste Water, 13th Edition, 1971 (APHA). 2. Annual Book of Standards, Part 23, Water Atmospheric Analysis, 1972 (ASTM). 3. Methods for Chemical Analysis of Water and Wastes, 1971, (EPA).

These sources often provide precision and accuracy estimates. For mercury, standard deviations of 40 percent at 0.35ug/l by atomic absorption and for cadmium standard deviations of 22-73 percent by atomic absorption have been reported. Mercury and cadmium will form the initial thrust of our modest program in water pollution.

Plans include development of Standard Reference Materials for mercuy in water in the ppb range and for mixtures of Hg, Cd and other toxic metals in the same concentration range.

Among, the organics, the pollutants of special concern by the above criteria are PCB and cyanide and the pesticides, DDE, DDD, DDT, Aldrin, Dieldrin, Endrin, toxaphene. These pollutants are likely to be high priority items when we enter the organic phase of the water pollution program.

The manuscript was prepared and typed by B. Veronica Bowie.

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Manager, Measures for Air Quality

WILLIAM H. KIRCHHOFF
Deputy Manager
Measures for Air Quality

1. Effect of Polymeric Structure on the Permeation Rate of Sulfur Dioxide

Project Leader D. H. Reneker, Polymer Division
Other Personnel G. M. Martin and J. D. Barnes

Objective

Standard Reference Materials 1625, 1626 and 1627 are sulfur dioxide permeation tubes of lengths ten, five and two centimeters.respectively. These tubes are intended for standardization of apparatus and procedures used in air pollution and related chemical analysis. The tubes are fabricated by sealing liquid SO_2 into a length of tubing made from tetrafluoroethylene-hexafluoropropylene copolymer. The equilibrium rate at which sulfur dioxide permeates the wall of a particular tube has been found to depend only on the ambient temperature [1]. However, the differences in permeation rate between tubes made in the same way from stock fluorcarbon tubing are so large that the extra work of individual calibration of each tube by a weighing procedure is necessary. The observed variation in permeation rate at 25°C for a typical batch of 50 permeation tubes was about ± 10% from the mean. This variation was much larger than would be expected if the dimensions of the tube were reasonably close to the nominal values. In addition, during calibration of a batch of tubes in which the sequence of the tubes along the stock tubing was recorded, it was observed [2] that the permeation rate fluctuated periodically so that a complete cycle of this variation occurred in a length of stock tubing corresponding to thirty

[1] Figures that appear as superscript indicate the literature references at the end of some of the sections.

five-centimeter long tubes. The amplitude of this periodic fluctuation in the permeation rate was also about ± 10%.

Since each SRM tube was calibrated individually, the use of the tubes was not affected by this variation within a batch. Therefore, the cause of this observed variation in permeation rate was not determined before these devices were issued as SRMs. Periodic variations in the dimensions of the tube were suspected as a cause for the variation in permeation rate. There was also concern that other parameters, mainly morphological, which are not generally controlled during extrusion processing might cause variations of the sort observed. Certain parameters that describe the morphology of crystalline polymers are known to affect the permeation rate through crystalline polymers [3]. The investigation described here was undertaken to identify the uncontrolled parameters in the process by which the permeation tubes were manufactured. Control of all important variables would allow the tubes to be calibrated on a batch basis and thereby reduce their cost. Also it is undesirable to have poorly understood and uncontrolled fluctuations in an SRM, even though individual calibration eliminates the undesirable effects of the fluctuations.

Approach

This investigation encompasses the tube dimensions, that is, length, inner and outer diameter, as well as the ellipticity and eccentricity of the inner and outer walls of the tube. The density of the polymer, which is known to be a function of the detailed thermal and mechanical history that the tube experienced during extrusion, was investigated. Morphological features such as birefringence, perferred orientation of the lamellar crystallites and variations in these features along a radial direction through the

wall of the tube were also studied. Other possible sources of variation such as the presence of hydrocarbon impurities in the polymer, pinholes and stress cracking were not included in this investigation. No obvious flaws in the tubes were seen. Pinholes or leaks around the plugs would produce a much higher rate of loss, which would be detected when the tubes were calibrated. This polymer is not likely to be porous or contain pinholes [4].

Progress

An excellent (negative) correlation of permeation rate with density was observed. Previous observations of the permeation rate of small molecules through polymers showed that small variations in density produce much larger variations in permeation rate. The only theoretical estimates available for the relation between density and permeation rate are based on an over simplified two phase crystalline-amorphous model of morphology. These theories, which have been successful in fitting data from some polymer systems, suggest that the variations in density observed here are not large enough to account entirely for the observed variation in permeation rate.

The observed variations in physical dimensions were much too small to account for the observed variations in permeation rate. The observed length variation was not only too small but uncorrelated with permeation rate. Some negative correlation with the inner and outer radius was observed but the observed variation in these dimensions accounts for only 1/15 of the observed variation in permeation rate. The observed variations in eccentricity and ellipticity of the inner and outer walls were small and not correlated with variations in permeation rate. The weight per unit length of the tube correlated with the

permeation rate largely because this parameter involves the density of the polymer and as noted above the density is correlated with the rate. The weight per unit length varies slightly more than the density suggesting some correlated changes in the radial dimensions. These conclusions are supported by a multiple linear regression analysis of the more important parameters.

Since the observed variations in density and physical dimensions of the tube account for only part of the observed variation in permeation rate, it appears probable that variations in the morphology of the crystallites of which the polymer is composed must also be present. This morphology determines the paths available to the permeation molecule and this affects the permeation. Morphological observations made on these tubes showed a variation in orientation of crystallites in different parts of the tube. Small morphological variations were observed between different tubes. These variations, which are probably caused by differences in thermo-mechanical history, can reasonably be expected to account for a significant part of the observed variation in permeation rate. However, quantitative measurements of these morphological features have not yet been made with sufficient accuracy to prove this.

REFERENCES

1. NBS Technical Note 545 (December, 1970) pps. 930.
2. Figure 9, p. 29 in reference 1.
3. R. K. Eby, Jour. Appl. Phys., Vol. 35, No. 9 pages 2720-24 (1964).
4. Dupont Polychemicals Department Information Bulletin No. X-90A page 3.

2. Development of Equipment and Test Materials for the Evaluation of the Reliability of SO_2 Measurements

Project Leader — John K. Taylor, Analytical Chemistry Division

Other Personnel — Erle R. Deadorff, Ernest E. Hughes, Rolf A. Paulson

Objective

To develop a system for generation of accurate concentrations of SO_2 in air, that would be useful to evaluate the performance of analytical methods and monitoring instrumentation; to develop test materials to evaluate the reliability of measurements of SO_2 in the air, using the EPA reference method.

Approach

The gas generation system makes use of an NBS-SRM permeation tube and a means to control the flow of an air stream to produce SO_2-air mixtures in a manifold. By selection of appropriate parameters, SO_2 concentrations ranging from 0.02 ppm to 1 ppm may be produced.

The test materials consist of ampoules containing measured amounts of sodium sulfite. The quantities are chosen to be equivalent to the amount of SO_2 that would be collected during a 24-hour sampling period using the reference method as described in the Federal Register, Vol. 36, No. 158, Page 15486, August 14, 1971 (PRA method).

Progress

The project has been completed and the details have been

described in a Final Report to EPA, dated September 19, 1972. The essential details are given in the following sections.

GAS GENERATION SYSTEM

The gas generation system was constructed from readily available sub-units, except for the permeation tube chamber. A diagramatic sketch of the system is shown in Figure 2.1. The system was housed in a metal cabinet 15 x 20 x 22, in. and can be easily carried from one location to another. It contains its own water bath for controlling the temperature of the permeation tube but requires connection to a cold water supply if the temperature is to be maintained at or below ambient.

The flow meters were calibrated to an accuracy of 1 percent and the temperature can be maintained to at least 0.1°C. Accordingly, it should be possible to generate an SO_2 concentration with a reliability consistent with these measurements.

The system was performance tested by analysis of the manifold gas using the PRA method. By use of suitable combinations of either a 2 cm or 5 cm permeation tube and adjustment of flow rate, concentrations in the range 0.02 to 1.14 ppm were produced. A least squares fit of predicted concentration with respect to analytical values, showed agreement within 2 percent which is well within the analytical uncertainty.

SULFUR DIOXIDE REFERENCE MATERIALS

Initial experiments were carried out in an attempt to develop aqueous solutions containing SO_2 that would

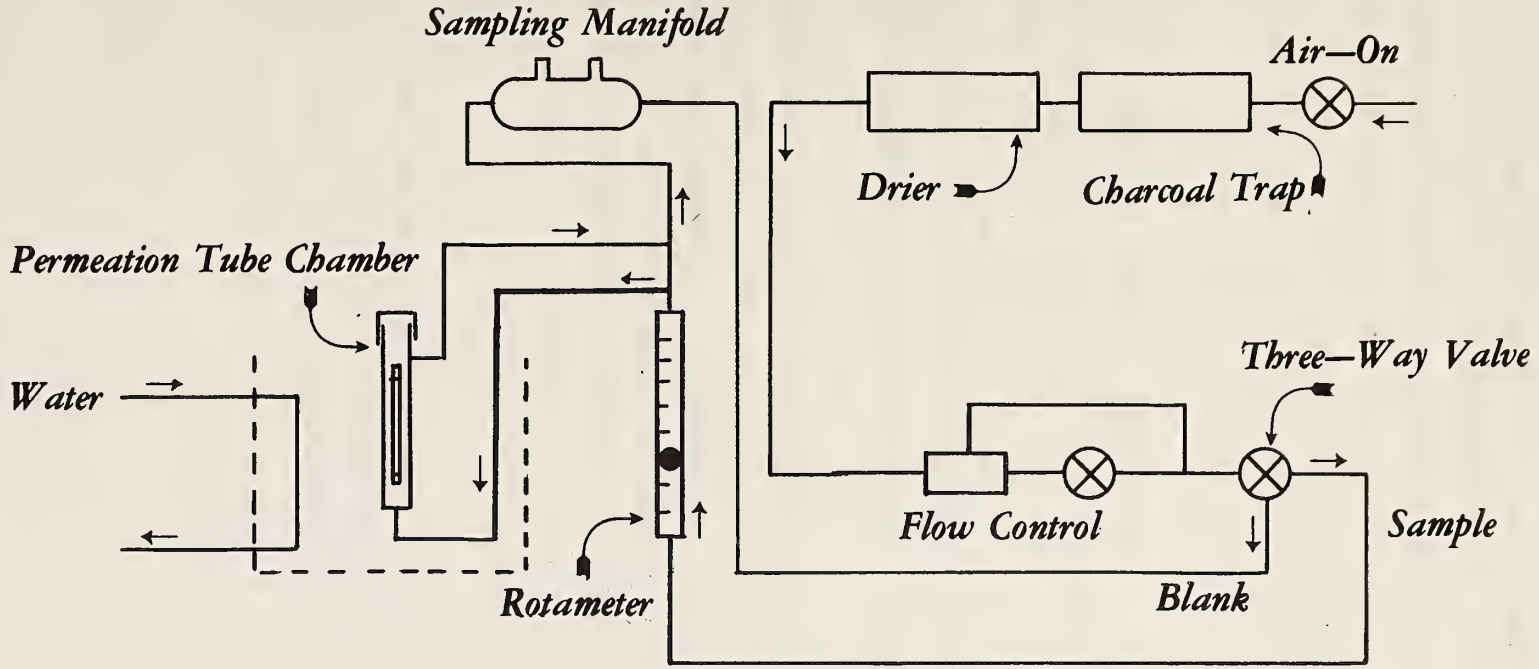

Figure 2.1, Gas Generation System

simulate the composition of a typical absorber. Such solutions decrease in concentration at the rate of about 1.5 percent per day of storage. Attempts to preserve them by sealing in ampoules in a nitrogen atmosphere and by addition of inhibitors such as mannitol were unsuccessful. The only satisfactory procedure found was low temperature storage which is not a feasible approach.

The method of R.C. Paule [Anal. Chem. 44, 1537 (1972)] consisting of encapsulating SO_2 in precision-bore capillary tubes was studied. Tubes of this type were prepared and used to introduce SO_2 into the absorber solution. Excellent results were obtained but the method was considered to be too cumbersome for routine quality control purposes.

The procedure finally developed consisted of powder samples, containing small amounts of sodium sulfite in an inert solid diluent, namely mannitol. A pre-weighed sample containing a definite amount of sulfite can be emptied into the absorber solution to simulate an atmospheric sample, which can be analyzed by a laboratory to evaluate its analytical proficiency.

A total of 800 sets of such samples containing 5 levels of SO_2 were prepared for EPA for the study. Twenty samples were selected from the production lot at each level and analyzed at NBS to ascertain the SO_2 levels, with the results summarized in Table 2.1.

Table 2.1

SO_2 Test Samples

µg SO_2/sample (lg)

Series	Average	c.i. Average	s Single
1000	14.3	0.8	1.9
2000	41.8	1.6	3.5
3000	120.4	2.7	5.7
4000	190.4	3.3	7.2
5000	242.1	3.7	7.8

The standard deviations, s, and confidence intervals, c.i., include uncertainties due to both analysis and inhomogeneity of mixing of the material. These samples were sent to EPA and were used in an extensive quality control evaluation study. The results of this study were reported in "Survey of Laboratory Performance -- Analysis of Simulated Ambient SO_2 Bubbler Samples", by S. M. Bromberg, G. K. Akland, and John C. Puzak, EPA No. 73-154, March, 1973.

Reference materials of this type have definite merit for quality control purposes. When used as a set, and the analytical values compared with the certified values, a slope of 1.00 ± 0.03 is expected. Values outside of this range are cause for quality control measures.

3. Fluorescence Detection of SO_2 in Air at the Parts Per Billion Level

Project Leader - H. Okabe, Physical Chemistry Division
Other Personnel - F. P. Schwarz, IMR, J. K. Whittaker

Objective

To extend the detection limit of the previously developed SO_2 fluorescence monitor downwards to the parts per billion level.

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1. H. Okabe, P. L. Splitstone and Joseph J. Ball, J. Air Poll. Control Assn, 23, 514 (1973)

Approach

The principle of detection is based on photon counting of the SO_2 fluorescence excited by the Zn 213.8 nm line. Fluctuation of the lamp intensity is accounted for by measuring the the ratio of the number of fluorescence photo counts to that of the excitation source.

Progress

At 8.6 ppb, the standard deviation is 29% for a counting time of about 1 minute. The detector response is linear from at least 8.6 ppb to 1.8 ppm. The major source of measurement error at low ppb concentrations is the statistical fluctuation of the low scattered light and signal counts, whereas at high SO_2 levels it is due to fluctuations in the sample preparation. The cell design was modified to reduce the scattered light. The inside of the cell was coated with a non-water-absorbing black Teflon to

reduce possible H_2O-SO_2-wall interactions. With the Zn lamp as an excitation source the quenching effect of water vapor on the SO_2 fluorescence signal previously observed with Cd 228.8 nm was found to be negligible. The result can be reasonably explained by the shorter life time of the SO_2 fluorescence.

A similar technique has been used to detect NO_2 in air. In this case, however, the detection limit would be in the ppm range with a glow discharge light source such as Hg, because of the efficient quenching of NO_2 fluorescence by air. On the other hand, a detector with a Zn light source may be used to detect ppb NO in pure N_2 since it is known that N_2 even at one atmosphere does not appreciably quench NO $A^2\Sigma$ state produced by absorption of the 213.8 nm line. The sensitivity will be greatly reduced if NO in air mixtures are tested because O_2 is known to be an efficient quencher of NO $A^2\Sigma$. Such studies are in progress.

4. Ultraviolet NO Detector (FY 1972 Project)

Project Leader W. Braun, Physical Chemistry Division
Other Personnel Prof. H. P. Broida, U. of Calif., Santa Barbara

Objective

To develop a UV optical detector for NO in air or nitrogen at levels below 1 ppm and to assess the relative merits of the various optical methods.

Approach

(A) The light source is an NO lamp. Absorption is measured in the region of small absorption where the absorbed light is approximately proportioned to the NO concentration. (B) Absorption is measured directly by an optoacoustic detector (C) Measurement of NO fluorescence in which selection of the exciting wavelength is done by means of a filter or a monochromator.

Progress

1. An NO resonance lamp with maximum output and minimum reversal was developed. The NO resonance radiation (light source) was isolated by a monochromator. The detectability limit for a 3 cm path length was determined to be about 10 ppm (with about 5% absorption) using simple DC detection. Differential phase sensitive detection would extend this measurement to $\sim$ 1 ppm. With 10x longer path lengths 0.1 ppm can easily be obtained. This additional complexity suggests that fluorescence measurement may result in a simpler and more sensitive device.

2. U.V. absorption of NO resonance radiation not isolated by monochromator: Absorption measurement by means of acoustic detection (Kreuzer detector). For this measurement a non-coherent source appears to present many problems. The limit of detection is about 100 ppm (with difficulty). This detection method was abandoned. 3. U.V. absorption of NO resonance radiation and measurement of NO fluorescence. The NO (1,0) 215 nm resonance line was isolated by means of a dielectric filter. Fluorescence was measured at right angles. Several collimating designs were developed and checked and an optimum design was developed. Dielectric filters were evaluated and it was found that, in the u.v., these filters are low (<10%) in transmission. The detection limit is probably as low as 0.1 ppb for NO in N_2. A similar method involves isolating the exciting line (0,0) or (1,0) at 225 and 215 nm from an emission line at higher wavelengths by means of a monochromator. Measurement requires developing a high speed monochromator. A preliminary approach was designed and several bread board experiments were performed. The project was terminated.

5. Gas Standards For Air Pollution Analysis

Project Leader Ernest E. Hughes
Other Personnel W. E. Dorko, E. C. Kuehner, W. P. Schedie
R. J. Joseph, J. K. Taylor

Objective

This project is concerned with the development of Standard Reference Materials for air pollution analysis, to provide traceability, through NBS, of all pollution related measurements to a common set of analytical standards. Auto exhaust emission standards formed the focus of this year's activity.

Approach

Research is conducted to provide gas mixtures meeting the three prime requirements of SRM's: accuracy; stability; ready availability. Accuracy requires the existence or development of an absolute method of analysis, or of an absolute method for preparation of primary standards. Stability requires that long term data be available on the particular gas system in the container in which it will be furnished. Availability requires the development of specifications for production of the gas in sufficient quantity to serve the needs of potential users.

Progress

Earlier research has made possible the certification of the following SRM's: carbon dioxide in nitrogen, SRM 1601-1602-1603;oxygen in nitrogen, SRM 1606-1607-1608-1609; hydrocarbon (methane) in air, SRM 1611-1612-1613; SO_2 permeation tube, SRM 1625-2626-1627. Details of the past

year's activities are described below.

PROPANE-IN-AIR

Propane standards in the range from 3 to 1000 ppm have been studied in detail and their stability in terms of time and total cylinder pressure is excellent. Primary standards can be prepared by gravimetric techniques with accuracy of ±1 percent at concentrations above 10 ppm. A gas chromatographic procedure has been developed for intercomparison of standards with a precision of one part in a thousand. Specifications for SRM production were prepared and cylinders of gas were produced by a commercial supplier. SRM's have been certified as follows:

Propane-Air SRM's

SRM No.	Propane Concentration, ppm
1665	2.8
1666	9.5
1667	48
1668	95
1669	475

These SRM's were prepared with the special requirements of automobile emission measurements in mind, but may be useful for other purposes as well.

CARBON DIOXIDE IN NITROGEN

SRM's of this kind offer no special problems. The stability is excellent and no problems were encountered in the certification analysis.

Carbon dioxide in this Standard Reference Material was determined by comparison with a secondary standard that had previously been intercompared with a set of gravimetric primary standards.

The imprecision of intercomparison is less than 0.3 percent of the concentration of carbon dioxide. The method of intercomparison was gas chromatography using thermal conductivity determination of carbon dioxide. The gravimetric standards against which the secondary standard was analyzed were prepared at such concentrations and in such numbers that non-linearity of the thermal conductivity detection was minimized. The limits of inaccuracy represent the uncertainty in the concentration of carbon dioxide in the gravimetric primary standards.

SRM's have been certified as follows:

Carbon Dioxide-in-Nitrogen SRM's

SRM No.	CO_2 Concentration, Mole Percent
1673	0.95
1674	7.2
1675	14.2

CARBON MONOXIDE

The major difficulty associated with these standards is the tendency for the concentration to decrease with time, especially at low concentration levels. Storage in stainless steel cylinders is a solution to the problem but this is not economically feasible for SRM purposes. A simple treatment of mild steel cylinders, consisting of applying a thin coating of ceresin wax to the interior surface, is

very effective. The wax is applied hot, to a heated cylinder which is subsquently allowed to drain and cool. SRM's for issuance in the near future have been prepared by a commercial supplier, using this technique according to an NBS specification.

The analytical procedure for measurement of CO after catalytic reduction to methane, has been improved to the point that intercomparisons precise to a part in a thousand are easily obtained. The certification analysis will be done by comparison with gravimetric standards prepared in stainless steel cylinders, which are adequate for this purpose.

SRM's containing CO in nitrogen became available in the fall of 1973.

NITRIC OXIDE

Some progress has been made in preparing SRM's consisting of nitric oxide in nitrogen but problems of instability remain. This appears to be due to adsorbtion of NO on the cylinder walls which is differentially released as the pressure drops in the cylinder during use. Pre-treatment of the cylinder with high concentration of NO, seems to minimize the difficulty, so an adequate solution to the problem appears imminent.

Chemiluminescent measurements of the SRM's with reference to gravimetric standards will be used for certification and the results will be correlated with absolute measurements under development elsewhere within NBS (See project 6).

OTHER STANDARDS

Studies are continuing on the stability of SO_2-air mixtures at high concentration. Cylinder pre-treatment and/or allowing sufficient time to equilibrate are solutions to the stability problem. The production of SRM's awaits clarification of the needs for such materials.

The NBS-developed ozone generator has been shown to be rugged and stable, and hence can provide an adequate means to calibrate oxidant measurements. A number of these generators have been constructed, calibrated, and used by EPA in their method evaluation studies. Several generators are maintained in continuous calibration in the NBS laboratory, using the neutral-Kl reference method. A simple procedure has been developed for comparison of an uncalibrated generator with respect to these, using the chemiluminescent method of measurement.

6. Absolute Coulometric Determination of NO

Project Leader — George Marinenko, Analytical Chemistry Division

Other Personnel — Dale Friend, Ryna Joseph, and W. Dorko

Objective

Accurate determination of NO and NO_2 in the parts per million concentration range for the purpose of confirming the integrity of automotive SRMs.

Approach

The chemical scheme employed in the analysis is as follows:

1. $2NO + 5H_2 \xrightarrow{\text{catalyst}} 2NH_3 + 2H_2O$

$2NO_2 + 7H_2 \xrightarrow{\text{catalyst}} 2NH_3 + 4H_2O$

2. $NH_3 + H_2O \longrightarrow (NH_4OH \rightleftarrows) NH_4^+ + OH^-$

The electrochemical measurement scheme is based on the anodic reaction

3. $2H_2O \longrightarrow O_2 + 4H^+ + 4e.$

The final stoichometric reaction is

4. $H^+ + OH^- \longrightarrow H_2O$

i.e. neutralization of ammonium hydroxide with electrogenerated sulfuric acid.

Progress

1. Measurement Aspects of Coulometric Determination of NO. Sampling of Gas - Two different methods of gas sampling were employed: (1) isolation of known volume of gas and (2) continuous flow of gas at a known rate.

C

Conversion of NO_x to NH_3 - An accurately measured volume of unknown gas is injected into a stream of hydrogen flowing in a specially built glass gas train. The injection of NO_x sample is performed under such conditions that the H_2/NO_x molar ration in the resulting mixture is at least 10^3. The mixture passes through the furnace where it undergoes reduction to NH_3 on a nichrome surface. Three different pieces of experimental evidence are offered as proof of 100% conversion efficiency.

(a) Using NO_2 permeation tubes the coulometrically determined leak rate is in agreement with the gravimetrically determined value.

(b) Mass spectrometric analysis of the reaction products after the NO-H_2 mixture is passed through the furnace, operated at different temperature also supports the quantitative conversion of NO to NH_3.

(c) Assay of "pure" NO coulometrically and the analysis of the same gas for impurities mass spectrometrically also support the accuracy of conversion and determination of NO:

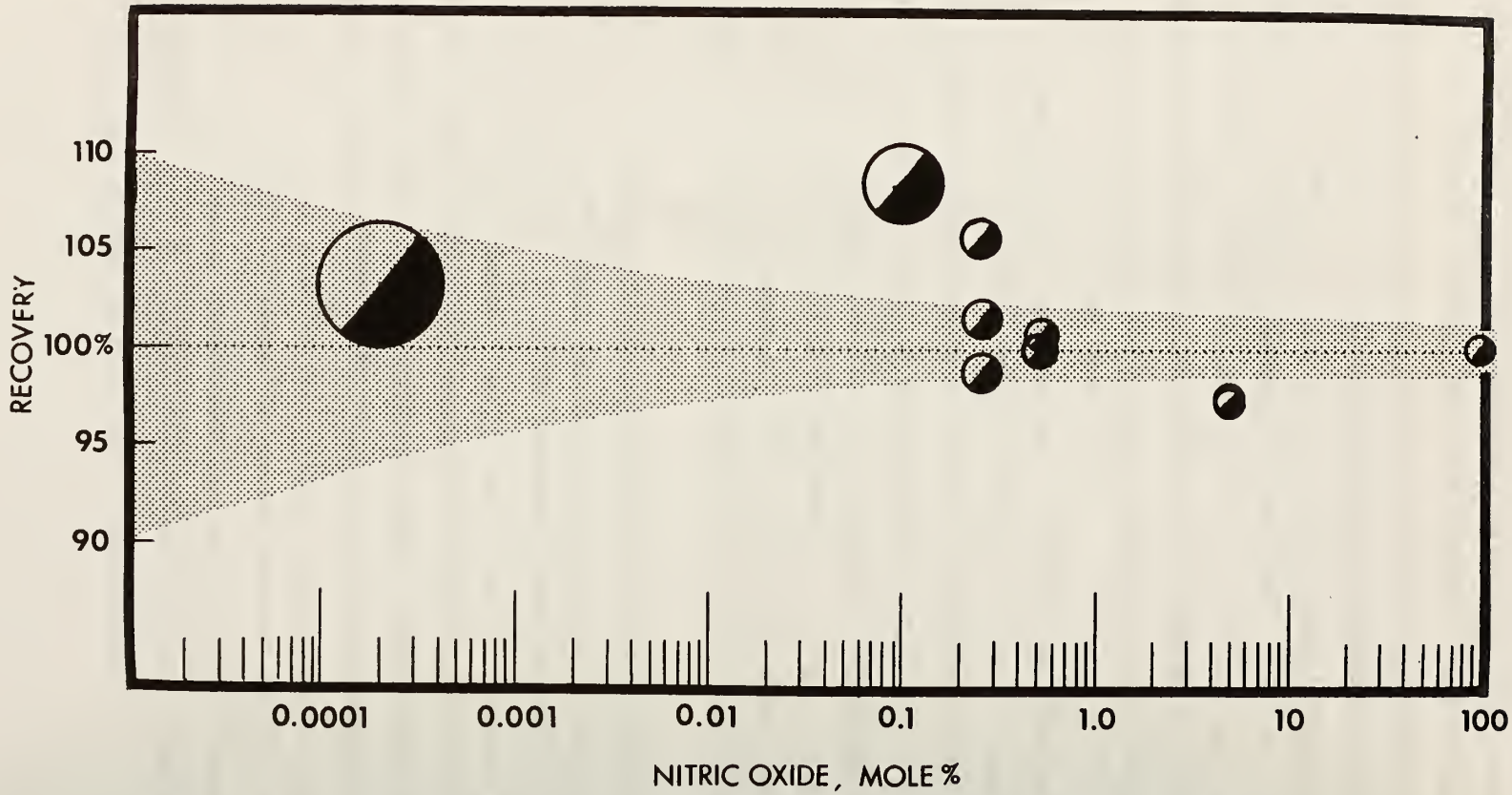
Coulometric assay	98.6%
Assay by difference	98.4%

The difference of 0.2% between the two values is well within the uncertainty of the two measurements.

Performance of gas train and coulometric recovery of ammonia. Pure ammonia was sampled by the (known) volume isolation method, injected into the gas train by displacement into hydrogen, passed through the gas train, absorbed in the electrolysis cell by the electrolyte and titrated coulometrically. The data obtained provide assurance that the gas system is operating properly, without losses, absorption of ammonia is efficient and thus the system can be used for accurate determination of NO and NO_2.

2. Determination of NO in Gravimetrically Prepared NO-N_2 Mixtures. - All samples in the 100% to 0.1% NO concentration range were analyzed by injection of a known volume of gas (25 cc) into the H_2 stream and titration of the absorbed ammonia. Below 0.1% NO,gas samples were continuously injected at a known rate and the flux balance method of analysis was employed. The results of analysis of known mixtures are summarized graphically in Figure 6.1.

The data obtained for NO-N_2 mixtures, covering six orders of magnitude concentration range, confirm absence of any systematic measurement error (bias). The examination of data clearly shows that significant differences exist between the measured and the calculated values of NO concentration. Moreover, even for mixtures of nominally the same NO concentration (e.g. 0.25%) differences between different preparations exist which are too large to be ascribed to the measurement error. Work is proceding in cooperation with the gravimetric preparation group in an effort to determine the cause of the observed descrepancies.



COULOMETRIC DETERMINATION OF NO

Figure 6.1

7. Nitrogen Dioxide Permeation Tube

Project Leader Ernest E. Hughes, Analytical Chemistry Division
Other Personnel Erle R. Deardorff

Objective

To develop a nitrogen dioxide permeation tube with improved characteristics of long term stability, increased service life, and low permeation rate, suitable for certification as a Standard Reference Material.

Approach

A permeation tube consisting of a small-area permeation sleeve attached to a larger glass reservior recently developed in this laboratory shows considerable promise. Mechanical improvements will be made, techniques for fabrication will be developed, and its stability and tolerance to stress of normal usage will be investigated.

Progress

At present the only practical means of preparing calibration mixtures of air and nitrogen dioxide at low concentrations is by means of permeation tubes. The two most serious objections to early nitrogen dioxide permeation tubes were that the rate decreased unpredicatably during the useful life of a tube, and that the rates of permeation were inconveniently high requiring high air flows to produce practical low concentrations. The problem of declining rate has been studied and found to be due to the increase in water content of the nitrogen dioxide as the total nitrogen dioxide decreases and is the result of water originally present in the nitrogen dioxide with which the

tube was filled and possibly to water which has permeated into the tube. A simple solution to the problem was found which resulted in a stable rate during the lifetime. This consists of including within the tube a small amount of phosphorous pentoxide which served to dry the initial charge and to eliminate the possible effect of permeation of water vapor into the tubes.

An alternative approach is to fill the tubes with anhydrous NO_2 under conditions to preclude moisture introduction. Tubes so constructed are under intensive investigation.

The design which appears to be most promising is shown in Figure 7.1. Tubes of this type have a service life of more than a year, are mechanically stable, and can survive temperatures above 40°C although there is some evidence that exposure to elevated temperatures for more than 8 hours may permanently change the characteristics of the Teflon and consequently the permeation rate. We have devised a very simple temperature indicator which accompanies the tube at any time when it is not in a controlled temperature environment. This consists of a crystalline mixture of $Zn(NO_3)2 \cdot 6H_2O$ and methyl red sealed in a short length of capillary melting tube. The mixture melts abruptly at 35°C and the difference between the physical appearance of a tube which has been exposed even briefly to temperature above 35°C and one that has not are quite striking. The rates of these devices can be controlled to some extent by adjusting the permeation area during fabrication and typical rates range from 0.6 to 2.5 mg/minute. Thus the air flow required to produce a concentration of 1 ppm is around 1 liter per minute or less.

NBS NITROGEN DIOXIDE PERMEATION DEVICE

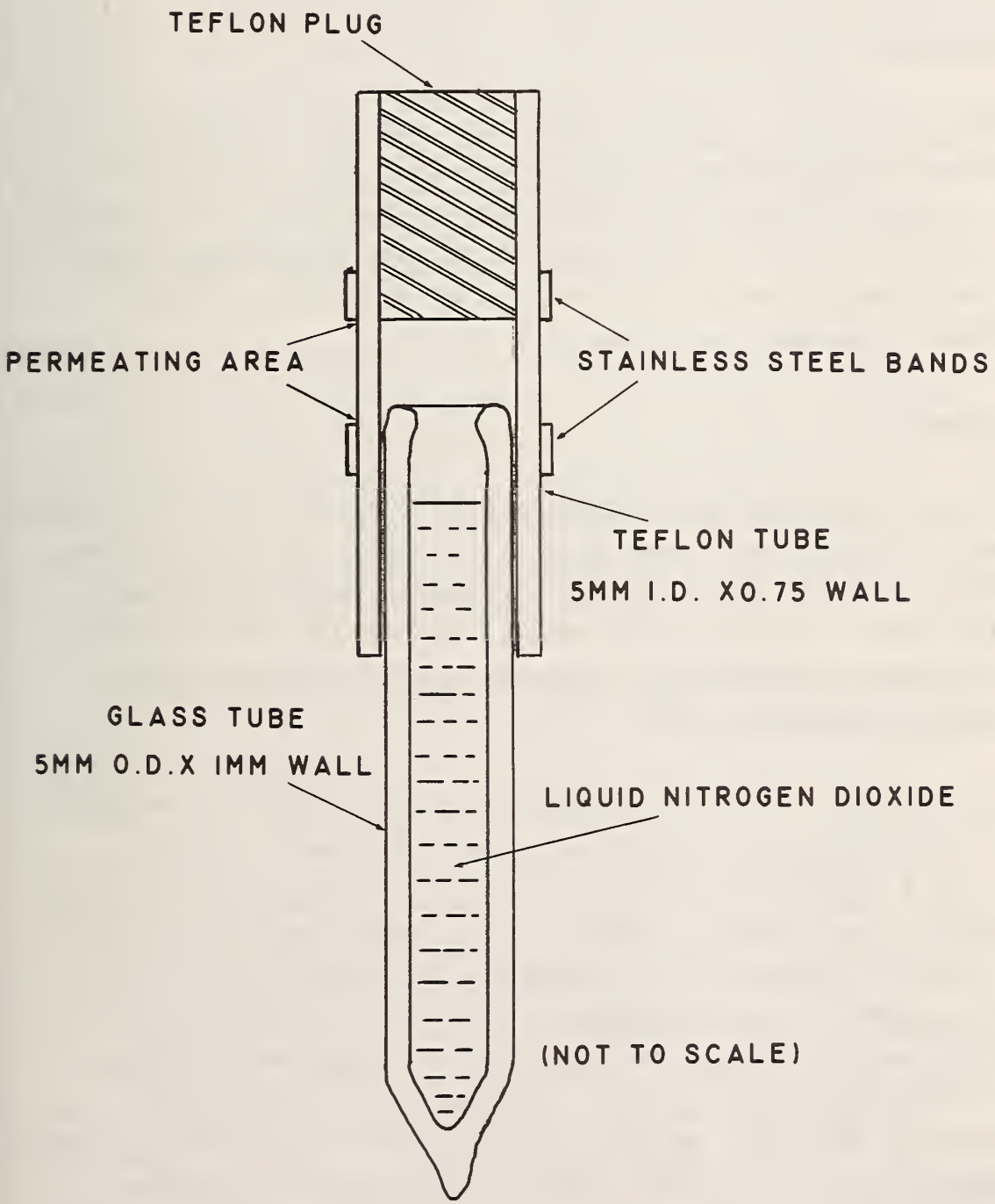


Figure 7.1 Improved design for a nitrogen dioxide permeation tube

8. IR Laser Detector for NO_x

Project Leader A. Kaldor, Optical Physics Division
Other Personnel A. Maki, S. Freund and W. Lafferty

Objective

Development of a simple, sensitive, specific, accurate and rapid measurement device to monitor the concentration of various pollutant molecules in gas samples, particularly NO and NO_2. This project aims to explore and develop ways in which molecular spectroscopy, and especially laser devices, can meet this need.

Approach

We have adopted a two-pronged approach as follows: (1) techniques are being developed to utilize laser devices in measuring air pollutants; (2) spectroscopic measurements are being made on pollutant molecules to provide back-up data for our own experimental program as well as experimental programs outside of NBS.

A. Construction and evaluation of an opto-acoustic detector. The opto-acoustic detector was built and tested using CO_2 as a radiation absorber and a CO_2 laser as a radiation source. The detector consists of a capacitance microphone. A number of different microphone configurations have been constructed. One particular microphone built with 0.0005" teflon coated with aluminum was most extensively tested. The microphone has 1/4" I.D. and had 2" active length. With this detector, using a 2 mm diameter laser beam, linear sensitivity for CO_2 from 1 ppm to 1000 ppm was observed. Above 1000 ppm rapid departure from linearity was observed.

Since this absorption is due to a hot band transition, rather than a fundamental it is quite weak. For a fundamental transition sensitivity is better by a factor of 100 to 1000. The repeatability of an absolute signal level from day to day was within 1%. The effect of particulates on signal fidelity was tested by the introduction of particulates (cigarette or cigar smoke) and was found to be devastating. Residual gas in the system was also found to be a serious problem in low concentration studies. Continuous flow experiments were a complete failure due to turbulance distorting the capacitor.

Presently the work has moved to the construction of a bakeable detector and this is now in progress. A number of materials are being tested. In connection with the application of this detector to the detection of NO a sealed CO laser is also under construction. The final design of this device has been frozen and its construction should be completed in the near future.

B. Measurement and analysis of high resolution infrared spectra of NO_2. In order to provide key information which was needed to interpret the strong fundamental band ν_3 (at 1600 cm^{-1}), the $2\nu_3$ band around 3200 cm^{-1} was measured and analyzed in detail. This analysis has revealed some interesting anomalies in the intensity distribution among the individual absorption lines in this band Such anomalies can lead to gross errors in estimating the absorption coefficient of NO_2 at a given wavelength from some overall low resolution intensity measurement. Similar anomalies also seem to be present in the ν_1, fundamental band of NO_2 around 1350 cm^{-1}. The work on the $2\nu_2$ band is now completed and is the subject of a paper which is now being written.

After the desired information was extracted from the $2\nu_3$ b band, it was a simple matter to calculate the spectrum of the ν_3 band. By comparing this calculated spectrum with the real spectrum measured at the Ohio State University, it was easy to make a detailed assignment observed spectrum. As a result of this assignment, a paper on the analysis of the ν_3, band of NO_2 is now being prepared in collobration with Prof. K. N. Rao and Dr. S. C. Hurlock of Ohio State University.

Since the NO_2 spectrum produced at Ohio State University was rather inferior by our standards, and since the NBS high resolution infrared spectrometer was not designed to operate below 1800 cm^{-1}, we are now in the process of collaborating with Prof. A. Cabana at the University of Sherbrooke on a re-examination of the ν_3, band of NO_2 at much better resolution.

The bending vibration of NO_2 (ν_2 at 750 cm^{-1}) is also being analyzed in collaboration with Prof. A. Cabana. The analysis of this band is more than half completed and should be finished in the next few months.

C. In order to understand and optimize later Zeeman experiments, a theoretical study of the Zeeman effect in NO_2 was undertaken. That study has been completed, and we now know in a qualitative sense just what sort of Zeeman effect to expect. Inititally we had feared that (as was the case with NO) only a few transitions would show very large Zeeman effects. We now know that is not the case although certain transitions will show a greater effect than others. The final step that remains is to actually perform some Zeeman modulation experiments and to compare the sensitivity for NO_2 measurement with that for NO.

D. In addition to the usual work on building and improving lasers, work has progressed on two important new devices, the spin-flip Raman laser and a Stark-shift and modulation cell for use in conjuction with any laser source. The demise of our CO laser tube has delayed work on the spin-flip laser, but work will resume as soon as a new CO laser is ready. In the meanwhile absorption measurements on ozone are being made with a CO_2 laser. That work, however, has just begun and will be reported at a later date.

Future Plans

The Zeeman modulated NO_2 measuring device will be tested and the sensitivity and linearity will be determined. Tests will also be made to determine if the presence of water vapor has significant effect on the sensitivity. A Stark modulated absorption cell which is now under construction will be tested on formaldehyde. A Stark modulation technique may be useful for molecules exhibiting this effect. The interference from other molecules can be minimized by careful choice of both the d.c. Stark off-set and the laser frequency. This Stark absorption cell will initially be used with CO, CO_2, or N_2O fixed frequency lasers, but later it will be used with a tuneable spin-flip laser. The spin-flip Raman laser is almost completed and should be operational in a couple of months. Initial work on the spin-flip laser will probably center around the problems of frequency measurement and stability.

The work on the analysis of the infrared spectrum of NO_2, will be continued. In collaboration with the University of Sherbrooke, the strongest absorption band ν_3 is being remeasured and a preliminary analysis of the spectra taken at Ohio State University will be extended and improved.

The remaining fundamental band ν_1 will also be measured and analyzed as will some important combination bands.

The high resolution spectrum of ozone will be measured and analyzed. Absolute intensity measurements will be made on individual rotation-vibration absorption lines and the variation with rotational quantum numbers will be determined so that remote sensing laser devices can be more accurately calibrated.

9. Light Scattering Methods for the Determination of the Properties of Particulate Matter in Air

Project Leader — C. C. Gravatt, Jr., Polymer Division

Other Personnel — Ivo Allegrini guest worker at NBS from Consiglio Nazionale delle Richerche Laboratorio sull' Inguinamento Atmosferico Roma, Italy

Objective

This project involves the study of new light scattering methods to determine in essentially real time the properties of particulate matter in air. The properties investigated are the total number, size distribution, chemical composition (as related to the index of refraction), and non--spherical character of the particulate matter.

Approach

This project comprises an experimental and theoretical study of the light scattering properties of particulate matter with the aim of finding rapid techniques for its characterization. From simultaneous measurements of light intensities at several scattering angles as a single particle passes through a light beam it is possible to obtain size, shape, and index of refraction information.

Progress

1. Determination of Particle Size Distribution by Intensity Ratio Method. An instrument has been designed, built, calibrated and tested which sizes particulates by the intensity ratio technique. The basic concept involves the

simultaneous measurement of the intensity of light scattered by a single particle at two small scattering angles. The ratio of the two intensities is a direct measure of the size and is fairly independent of the index of refraction of the particle. The optical system consists of an argon ion laser source and an annular iris-fiber optic scattered light detector. The maximum count rate of the system is 20,000 particles/sec and the diameter range covered is 0.2μm to 4μm. The theoretical calculations on the intensity ratio method have been completed and they show that for the scattering angles of 10° and 5° this technique can size particles in the 0.2 μm to 4 μm range with an error no greater than ± 15% for all possible materials in air. In addition, optimum angular ratios and apertures have been determined for a wide range of size regions.

The conversion of the analog ratio light scattering instrument to a digital instrument with computer data acquisition and analysis is in progress.

2. Determination of Particle Size in the Range 0.05 μm to 0.5 μm. As an outgrowth of the theoretical work described in part 1 above, several methods were developed for the sizing of particles in the diameter range 0.05 μm to 0.5 μm with an index of refraction error no greater than ± 25% for all likely materials in air. All of these methods are based on a measurement of the intensity scattered at a single angle normalized by the intensity incident on the particle, and only require minor modification to the electronic system and no modification of the optical system.

3. Characterization of Particulates as to their Optical Absorbing Properties. A very simple method for distinguishing between optically absorbing particles, e.g. carbon

and metals, and non-absorbing particles was found from the theoretical studies. This involves a measurement of the absolute scattered intensity over the angular range 30° to 70°.

4. Detection of non-Sperical Particles. A preliminary theoretical study of the depolarized light scattering by lone rods has been performed. It appears that a measurement of the ratio I (depolarized)/I polarized would serve as a way of detecting asbestos particles.

Suggestions for future research: Listed below are several projects which appear to be attractive on the basis of what has been learned up to this time about the optical characterization of particulates. No attempt has been made to limit these suggestions only to air pollution studies.

1. Experimental verification of the detection of particles in the size range from 0.05 μm to 0.5 μm.

2. Experimental vertification of the characterization of particles as to their optical absorbing character.

3. Possibility of detecting particles smaller than 0.05 μm by ultra-fast single photon counting methods.

4. Studies of the kinetics and mechanisms of particle growth.

5. Studies of the kinetics and mechanisms of burning by monitoring the nature of the smoke. A possible result of this work would be improved smoke detectors.

6. Characterization of particulates and micro-organisms in liquid systems.

10. Instrumentation for Particle Sizing

Project Leader M. L. Greenough, Measurement Engineering Division

Other Personnel J. Cohen, E. C. Palasky

Objective

Instrumentation is being developed for determining the size of particles in the 0.1 to 5 micrometer diameter range, based upon the selective forward scattering of a light beam across which the particles are caused to flow.

Approach

The general approach follows that proposed and experimentally verified by Dr. C. C. Gravatt of NBS, Polymer Division. Specifically the goal is to detect the light scattered in narrow conical bands located at 5 degrees and at 10 degrees from the beam axis. The ratio of the light levels in the two bands is to be extracted for individual particles during transit. These ratio indications are to be summed in a small computer for periodic printout of numeric distribution according to particle size.

The system planned will be built around an argon ion laser whose beam is focused as it enters the sample cell. The air sample being measured will be passed through the cell, after being extracted from an overall intake manifold. When particles contained in the air pass through the narrow laser beam, the small amount of scattered light will be transmitted through a conical mask assembly called the director, to two photomultiplier tubes. These tubes will be the source of analog signal pulses whose relative

amplitudes during coincidence are predicted to be dependent upon size of the particle initiating the scattering. Detection is planned at a conical bands each one degree wide, at 5 and 10 degrees from the beam axis.

The pulse signals will be fed to an interface unit providing the interconnection between the optical signals and the computer. In the interface the 5-degree signal is to be applied to 32 threshold comparison circuits which have appropriate voltage dividers. To the other side of the comparison circuits will be applied the 10-degree signal. Whenever the 10-degree signal exceeds the threshold fraction of the 5-degree signal, a digital output is to be created. The output of the 32 comparison circuits is to be recoded in a computer word developed on the basis of one eight-bit byte for each discrete particle which is detected. Thus eight bits in the word convey the information regarding particle size. At the end of the pulse time this word will be transmitted out of the interface buffer to be accumulated in the computer's memory according to bit contents.

At periodic intervals, perhaps five minutes or as desired, the computer will print out a report giving the distribution of accumulated particle sizes, using the teletype unit which is to be a part of the computer system.

Physically the system plan calls for the above-mentioned elements to be mounted in a single rack about 45 inches high. On the top will be the sensing assembly including the laser, sample cell and photomultiplier tubes. At the front of the rack will be the interface, computer, and power supplies. If air-handling equipment is required, it will be mounted at the lower rear.

Progress

The major activities so far have been in mechanical design and in procurement of components. The former has been concentrated on the director and its associated optical chamber.

In the mechanical design a large part of the effort has been given to providing flexibility for future options. Two examples might be the provision for sensing at an angle of 45 degrees to the beam, and for splitting the 10-degree cone into its polarized components. While these options are not presently being incorporated, the design is being carried out insofar as possible in a manner so as to facilitate their ultimate inclusion. For this reason we have adopted an alternate approach to the fiber-optic conduction of light from the director to the photomultiplier tubes as used in the breadboard design. The planned arrangement involves simple lenses, together with mirrors and light baffles. An additional benefit should be greater transmission efficiency. An increase in efficiency at this point is directly translatable into a requirement for lower laser power, a feature which is valuable from the standpoints of economy and safety.

The new director has been designed as a series of baffles, a mechanically more complex assembly than the original tapered cones. This was done in an attempt to minimize possible effects from diffraction and grazing-angle reflections. The specific goal is to take all feasible precautions to eliminate as many sources of spurious signal as possible through careful restriction of the effective sensing zone in the sample cell. Construction of the director has been completed.

Calibration techniques are being studied for the instrument after installation in the field. Because of anticipated difficulty in arranging for the passage of a gas of known quantity and particle size, an alternative technique is desirable in order to verify or set calibration at frequent intervals. The currently favored plan for field calibration is to employ an insertable yoke containing a very fine tungsten wire. Prior calibration of the wire compared to known gas composition should then serve to provide the desired scaling factors.

11. Fossil Fuel Standards

Project Leader P. D. LaFleur, Analytical Chemistry Division
Other Personnel The services of many scientists throughout the Analytical Chemistry Division were employed.

Approach

Samples of coal, fly ash, gasoline and fuel oil were acquired and packaged. The sources and identification of the samples are as follows:

Coal and Fly Ash

Sample obtained from the Tennessee Valley Authority, Widow's Creek Steam Plant, Stevenson, Alabama. One sample of the coal from Widow's Creek was from the Fabius Mine in Fabius, Jackson County, Alabama and was washed. The fly ash sample associated with this coal was obtained from hoppers beneath centrifugal mechanical collectors. The other sample of coal was from Fies and Island Mine No. 9, Hopkins and McLean County, Kentucky (Western Kentucky). The coal was raw. The fly ash sample associated with this coal was taken from the hopper below an electrostatic precipitator.

A sample of coal from the Baltimore Gas and Electric Company, used at the H. A. Wagner Generating Station, was obtained from Nicholas County, West Virginia, from three separate mines. The fly ash associated with this sample was obtained from the hopper below an electrostatic precipitator.

A sample was obtained from the Commonwealth Edison Company from coal used at their Crawford Station in Chicago. The

source of the coal was a mixture of 80% colstrip from Montana and 20% a blend of colstrip and coal from Southern Illinois. The fly ash from this sample was also from an electrostatic precipitator.

The fifth sample of coal was obtained from the Potomac Electric Power Company and came from their Potomac River Station, Alexandria, Virginia. Exact location of the mines from which it was obtained is essentially impossible to determine since the coal came from the conveyor into the burner unit, but essentially all of the coal used at this Station is from West Virginia and eastern Kentucky. The fly ash associated with this coal was from an electrostatic precipitator.

The fly ash was sieved and that fraction which passed a 120 mesh standard sieve (125 μm) was taken for analysis. The entire sample was mixed in a large double cone mixer. Homogeneity was demonstrated using X-ray fluorescence analysis and neutron activation analysis.

The coal was reground (except for the PEPCO sample which was already fine enough) by Forrest Walker at the U.S. Bureau of Mines in Pittsburgh, Pennsylvania. The coal was sieved, and that portion passing through a 170 mesh (88 μm) standard sieve was taken for analysis. The entire sample was mixed in a large double cone mixer. Homogeneity was demonstrated using neutron activation techniques.

Residual Fuel Oil

The fuel oil sample was obtained from the Standard Oil Company of New Jersey and originated from their refinery at Aruba, Netherlands Antilles. This material meets all of the ASTM specifications for a #6 residual fuel. This

is the same material (although taken from bulk storage in a 55 gallon drum) as NBS Standard Reference Material 1622. Homogeneity was demonstrated with neutron activation analysis and gravimetry.

Gasoline

Gasoline samples were obtained from service station pumps in the Gaithersburg, Maryland area. Six samples were obtained from the following stations using metals cans:

American	Amoco Premium (lead free)
Shell	Shell of the Future (low lead)
Texaco	Regular
Gulf	Gulftane Low Lead
Citgo	Premium
Esso	Low Lead

Within 30 minutes of collection, the samples were transferred to a large polyethylene tank which had been cleaned previously with nitric acid. Homogeneity was demonstrated using atomic absorption spectrophotometry.

The analytical program, which has commenced, will be accom-- plished using the following methods.

	Coal	Fly Ash	Fuel Oil	Gasoline
Be	COL	COL	COL	COL
	ATA	ATA	ATA	ATA
F	DIS	DIS	N	N
V	ATA or COL	ATA or COL	ATA or COL	ATA or COL
	NAA	NAA	NAA	NAA
Cr	COL	COL	COL	COL
	NAA	NAA	NAA	NAA
Mn	ATA	ATA	ATA	ATA
	NAA	NAA	NAA	NAA
Ni	POL	POL	POL	POL
	SSM	SSM	SSM	SSM
Zn	ATA	ATA	ATA	ATA
	NAA	NAA	NAA	NAA
As	ATA or COL	ATA or COL	ATA or COL	ATA or COL
	NAA	NAA	NAA	NAA
Se	SSM	SSM	SSM	SSM
	NAA	NAA	NAA	NAA
Cd	SSM or ATA	SSM or ATA	SSM or ATA	SSM or ATA
	POL	POL	POL	POL
Hg	ATA	ATA	ATA	ATA
	NAA	NAA	NAA	NAA
Pb	POL or ATA	POL or ATA	POL or ATA	POL or ATA
	IDM	IDM	IDM	IDM
U	NAA	NAA	N	N
	IDM	IDM		
S	PPT	PPT	PPT	PPT

Key: ATA Atomic Absorption Spectrophotometry
COL Colorimetry
DIS Distillation
IDM Isotope Dilution Mass Spectrometry
NAA Neutron Activation Analysis
POL Polarography
PPT Precipitation

SSM Isotope Dilution Spark Source Mass Spectrometry
N Will not be determined

Progress

Results have been received from 32 laboratories who are participating in the intercomparison exercise on these samples. The current status of NBS measurements on these materials is as follows:

Element	Values-Technique	Probable Certified Value or (Information Value)
FLY ASH		µg/g
As	61.2±2.2 NAA 62±3 PAA	61±3
Be	12.4	(12)
Cd	1.43±0.04 NAA, 1.46±0.05 ATA, 1.45±0.05 IDSSMS	1.45+0.06
Co	38.0±0.6 NAA	(38)
Cr	131.6 ATA, 131.5 Atomic Flour.	132±5
Cu	124.5 IDSSMS, 112.1 COLOR	(120)
Hg	0.145±0.006 NAA	(0.15)
Mn	520±10 NAA, 493±10 ATA, 484±20 COLOR	495±30
Ni	100.8 IDSSMS, 101.8 COLOR, 98±1.5 POL, 96.6 IDMS	98±3
Pb	70.8±0.1 IDMS, 67.0±1.1 POL	70±2
Rb	112±1 IDMS	(112)
Se	9.1±0.2 NAA, 9.6±0.2 IDSSMS	9.3±1.0
Sr	1379±2 IDMS	(1380)
Tl	4.1±0.1 IDSSMS	(4)

Element	Values-Technique	Probable Certified Value or (Information Value)
FLY ASH		µg/g
Th	24.2±0.1 IDMS	(24)
U	11.6±0.1 IDMS	(11.6)
V	214±8 NAA, 214 REDOX	214±8
Zn	195±23 NAA, 216.1±2.4 ATA	210±20
COAL		
As	5.8±0.3 NAA, 6.1±0.4 PAA	5.9±0.4
Cd	0.23±0.02 NAA, 0.24 POL, 0.17±0.05 IDSSMS	0.23±0.03
Cr	23.4 COLOR, 20±2 ATA	22±2
Cu	18±2 IDSSMS, 18±1 ATA	18±2
Hg	0.11±0.01 NAA	(0.11)
Mn	46.4±0.6 NAA, 49 COLOR	47±3
Ni	14.8±0.1 POL, 15 PAA 14.80±0.05 IDMS	15±1
Pb	30±9 IDMS, 28.7±0.1 POL	30±9
Se	2.7±0.2 NAA, 2.99±0.2 IDSSMS	2.8±0.2
Tl	0.59±0.05 IDSSMS, 0.59±0.01 IDMS	0.59±0.05
Th	3.02±0.01 IDMS	(3)
U	1.39±0.02 IDMS, 1.3±0.1 NTT	1.4±0.1
V	35.5±1.8 NAA, 33.7 REDOX, 35±4 ATA	35±4
Zn	36.0±0.6 NAA 39±5 IDSSMS	37±4
FUEL OIL		
As	0.056±0.004 NAA	(0.06)
Fe	12.3±0.5 POL	(12)
Hg	0.002±0.0002 NAA	(0.002)
Mn	0.121±0.001 NAA	(0.12)
Ni	38±2 IDMS, 35.2±1.14 POL	37±3

Pb	0.041±0.005, IDMS, 0.041±0.005 POL	0.041±0.005
Se	0.138±0.06 NAA	(0.14)
Th	0.000026±0.000001 IDMS	(0.00003)
U	0.00004±0.00002 IDMS	(0.00004)
V	315±5 NAA	(315)
Zn	0.17±0.02 NAA	(0.2)

Key:

ATA = Atomic absorption
COLOR = Colorimetry
IDMS = Isotope dilution mass spectrometry
IDSSMS = Isotope dilution spark source mass spectrometry
NAA = Neutron activation analysis
PAA = Photon activation analysis
POL = Polarography
REDOX = Redox titrimetry
NTT = Nuclear Track Technique

12. X-Ray Fluorescence Analysis of Air Particulates

Project Leader K. F. J. Heinrich, Analytical Chemistry Division
Other Personnel R. Myklebust, C. E. Fiori, M. M. Darr

Objective

To investigate the use of x-ray fluorescence methods to obtain accurate and rapid analysis of particulate air pollutants on an economically attractive basis.

Approach

Recent advances in Si(Li) solid-state detectors (energy dispersive x-ray analysis) have brought their resolution and sensitivity into the range of practical usefulness to the analysis of air particulates. These advances provide an alternative to previously existing x-ray spectrometers, which accomplish wavelength dispersion by means of crystal monochromators. The developments in both techniques have produced uncertainty as to the relative merits of each arrangement in terms of sensitivity, accuracy and economy. We are performing experimental work using both techniques to provide a basis for comparing their characteristics and relative merits.

Progress

We have encountered problems obtaining well-characterized air particulates to be used as benchmarks in establishing the sensitivity, accuracy and efficiency of our methods. As an interim study, we have made tests using NBS Standard Reference Material 1571 Orchard Leaves. This powdered

material is well characterized for some of the elements of interest to air pollution studies, such as copper, zinc, and lead.

The initial tests indicate that the elements lying between manganese and lead can be detected to lower levels between 1 and 3 ppm when using wavelength dispersion. For energy dispersive x-ray analysis, similar levels have been reached when excitation is properly selected.

The arrangement of the equipment for energy dispersion was constructed at NBS. Experiments with it have pointed out several possible improvements over the present arrangement in sensitivity and stability. These changes in apparatus are now being made.

Some specimens of air particulates, for which chemical analyses will be available in September 1973, have been obtained and qualitatively analyzed. These, along with other materials that are becoming available, will provide more relevant standards with which to test x-ray methods.

In spite of the promising results with energy-dispersion equipment, we do not exclude the possibility that in the final analysis wavelength-dispersion techniques may be superior in resolution, sensitivity and cost. Therefore, we are contemplating an investigation of possible improvement in wavelength-dispersive equipment as well as for energy dispersion.

13. Airborne Quartz Measurement

Project Leader A. Perloff, Inorganic Materials Division
Other Personnel F. A. Mauer, C. Hubbard

Objective

Primarily to establish the detection limits and sensitivity of the conventional x-ray diffraction technique for the analysis of quartz in respirable dust samples collected by personal sampling devices. In addition, investigation of the feasibility of the energy dispersive technique as applied to the same samples.

Approach

The possible variables affecting the detection limits and sensitivity of the conventional x-ray technique are primarily:

1. Filter material.
2. Sample collection techniques.
3. Instrumentation effects.
4. Data measurement techniques.
5. Impurity effects.

Items 1 and 2 have been well established by other investigators and item 5 is a very variable effect dependent on the source of the sample. It was decided to concentrate on items 3 and 4 using silver membrane filters and both air and liquid deposition dust collection procedures to prepare a series of samples containing a known amount of pure, respirable sized, quartz dust. The major quartz peak was measured for these samples on various diffractometers with varying slit sizes and detector systems using both scanning and peak height techniques. From these measurements it should be possible to establish a minimum

detection limit and determine the sensitivity and reproducibility of a given diffractometer configuration.

After optimization of the energy dispersive equipment some of the same samples would be measured with this technique to establish its limitations and feasibility as an analytical tool for quartz dust samples.

Progress

The most recent standard curves indicate that the major peak of pure quartz is observable at a peak to background ratio of 2 in a 20 µg sample air deposited on 25 mm Ag membrane filters (surface density 5.3 $\mu g/cm^2$) utilizing conventional diffractometer equipment and commonly available slits. Varying receiving slits has minor influence on the peak to background ratio. The choice of slits would be a compromise between lower background rates and sufficient counts.

The air deposition samples appear to provide a better uniformity of sample density and a linear calibration curve through the origin. The wet filtration samples appear to have greater variation in reproducibility and possibly a non-linear calibration curve. If the wet filtration procedure is to become the standard method, further work on it is indicated.

The comparison of detectors shows that the highest sensitivity(net counts per microgram of quartz) is obtained with the solid state detector because its energy resolution permits elimination of the β lines without the use of a filter which normally introduces an attenuation of 50%. However, this detector is too complex and costly for general

use. The scintillation detector is recommended for general use. The proportional counter appears to have no advantage that offsets its poor count rate linearity and poor noise rejection.

Fourier transform theory has been applied to powder diffraction peaks in order to resolve composite peaks. Preliminary results indicate that the full width at half maxima (FWHM) of peaks in the conventional pattern is twice the FWHM of peaks in the resolution-improved spectrum. A composite of two diffraction peaks with $\Delta 2\theta = 0.024°$ appears to be a single peak in the original recorded pattern. The resolution improved pattern clearly reveals the existence of two peaks. Future extensions of the program will provide intensity measurements of each component of the spectrum. We think that the preliminary results of the new deconvolution-of-peaks technique are very encouraging. The method offers promise of improved analysis accuracy not only for quartz but for any case of overlapping diffraction peaks such as asbestos and its associated matrix minerals.

The energy dispersive technique has some attractive features for bulk samples, but it is not a feasible alternative for the quantitative analysis of respirable quartz at the low levels of the present threshold limit value requirements.

14. Polycyclic Aromatic Hydrocarbons in Air Borne Particulates

Project Leader Charles P. Talley, Analytical Chemistry Division

Other Personnel Rosalie M. Angeles, Stuart P. Cram

Objective

To make a preliminary investigation of the feasibility of using high performance liquid chromatography (HPLC) for the measurement of polycyclic aromatic hydrocarbons on air-borne particulate matter.

To investigate the potential sample handling and analysis problems, and suggest future work. Project was limited to one (1) man-month.

Approach

The aromatic hydrocarbons on air borne particulates have traditionally been determined as a group by complex, nonselective, and time consuming methods utilizing soxhlet extraction, conventional column chromatography, and absorption spectrophotometry of isolated fractions. Such a procedure could require as much as a one man-week effort for each analysis and at best result in semi-quatitative data. The advent of HPLC has added a new dimension to the speed, efficiency, specificity, and accuracy with which cromatographic separations and analyses can be accomplished. High efficiency chromatographic column materials ($\leq 50\mu m$) and microvolume ultra-violet detectors sensitive to one nanogram have increased the sensitivity and selectivity of analysis and eliminated the cumbersone and macro-level measurement methods. These methods have been implemented for the current study and appear to be the method of choice

for the analysis of trace amounts of nonvolatile organic compounds.

Progress

The extraction and isolation procedure used followed a scheme reported in the literature [Closson, A., Nicotra, C., Perilhon, and Cornu, A., Pollut. Atmos., 12, 239 (1970)] which replaced the rigorous 24 hour soxhlet extraction with a mild one-hour leaching aided by ultrasonic agitation. This extraction was followed by a series of solvent extractions which separated the polycyclic aromatics from the other organics which were also leached from a New York City filter dust sample.

The final extract was subsequently concentrated and an aliquot equivalent to the extract from 3 mg of air particulates was subjected to reversed phase chromatography. The following experimental conditions were used for the separation:

Column: 2m x 2.1 mm Corasil-C_{18}
Mobile Phase: Methanol/Water/Acentonitrile = 3/2/1
Flow Rate: 0.32 ml/min
Detector: 8µl UV cell (b = 1.0 cm) at 254 nm.

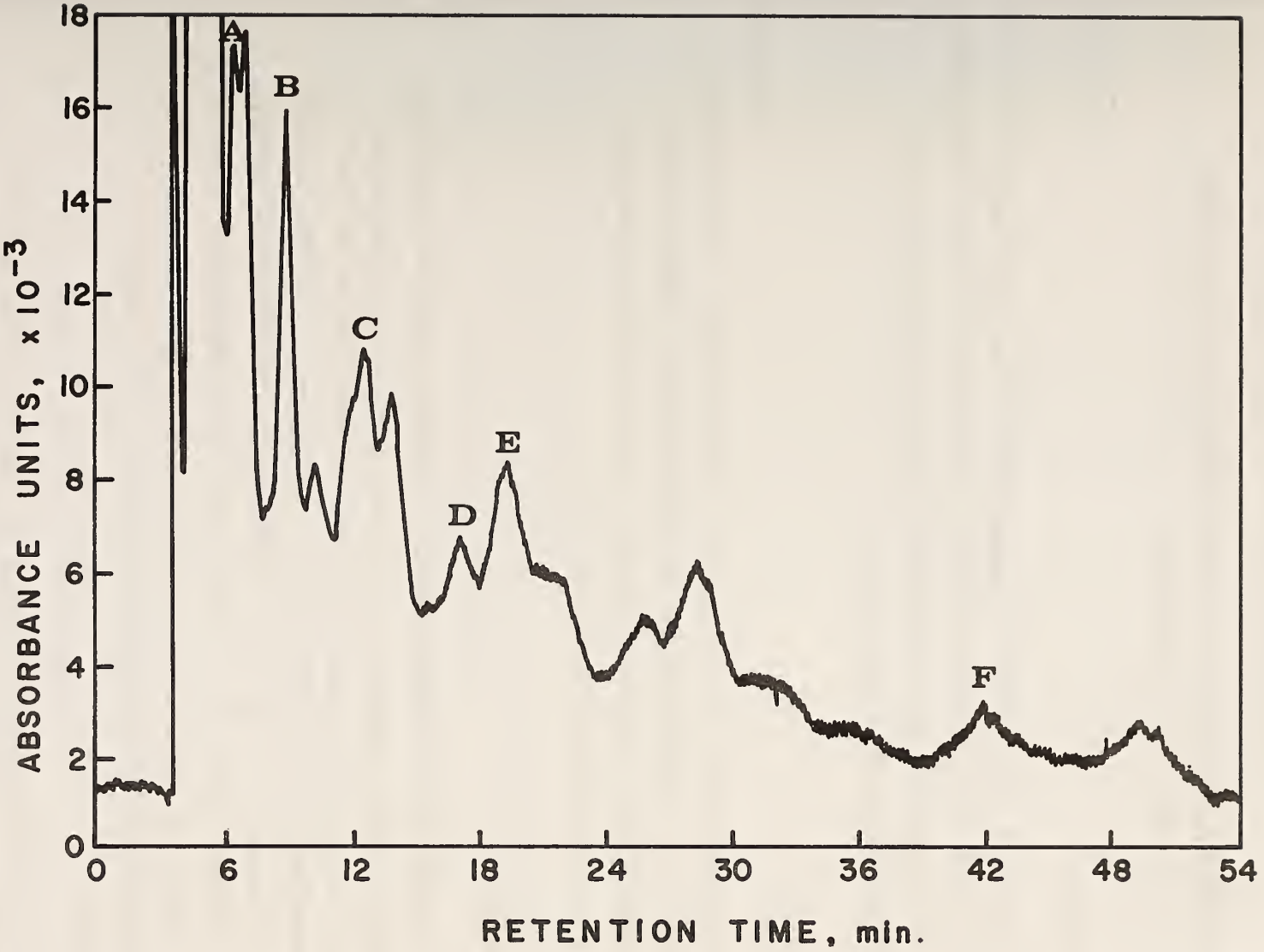
Figure 14.1 is a typical chromatogram resulting from this procedure after optimization of the separation conditions. More than 15 different peaks are discernible from this analysis, and six have been tentatively identified by comparison of their retention volumes with those of known standards. Those identified are labeled as follows:

A. Biphenyl
B. Naphthalene
C. Phenanthene
D. Fluoranthrene
E. Pyrene
F. Chrysene

Future Work

The accuracy and precision of the total procedure including isolation and chromatography as applied to the problem of aromatics in air particulates must be rigorously established. The identity of all discernible peaks must be confirmed by fraction collection and measurement utilizing other techniques such as infra-red spectrophotometry, mass spectrometry, and nuclear magnetic resonance spectroscopy. Then meaningful measurements at the subpart per million level can be made.

HPLC with ultrasonic extraction has been shown to be a potentially rapid, selective, and sensitive method of analysis for polycyclic aromatic hydrocarbons in air borne particulate matter.


A
B
C
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E
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ABSORBANCE UNITS, x 10⁻³
RETENTION TIME, min.
0
2
4
6
8
10
12
14
16
18
0
6
12
18
24
30
36
42
48
54

Figure 14.1

15. Particle Dispersion in a Gas

Project Leader H. J. M. Hanley, Cryogenics Division
Other Personnel S. Jarvis, Jr.

Objective

To conduct a theoretical assessment of the importance of microscopic molecular diffusion as a mechanism for dispersion of pollutants in air relative to other mechanisms such as turbulence and convection.

Approach

The kinetic theory of gases is used to study the dispersion mechanism. The treatment is sufficiently general that the results are applicable not only to gaseous mixtures but also to gas-particle mixtures.

Progress

The dispersion of particles in a gaseous medium has been studied with respect to the ratio of a mean particle radius (r) to the mean free path of the gas molecules (λ). A parameter, s, is defined by the relation $s=r/10\lambda$ which is equivalent to $(10\ K_n)^{-1}$ where K_n is the Knudsen number. We indicate that if $s<1$, the particle dispersion follows the diffusion laws of kinetic theory. An equation to determine the dispersion velocity for all values of s is proposed.

The calculations are related to particle dispersion in the atmosphere and it is suggested that diffusion can contribute to an overall dispersion mechanism, even if convection is present in the atmosphere.

16. Urban Particlate Sample

Project Leader W. H. Kirchhoff, Measures for Air Quality
Other Personnel J. K. Taylor, W. Cassatt

Objective

Collection of two 50 lb. samples of airborne urban particulates, one from the St. Louis vicinity and one from the Los Angeles vicinity. This material will ultimately be used as a Standard Reference Material for urban particulate analysis.

Approach

The following tasks are delineated:

1. Site selection
2. Provide as collection equipment:
   a. Fabric filters with 80% collection efficiency for particles 0.3-3 micrometers diameter.
   b. Prefilter to remove particles of greater than 10 micrometers.
   c. A 30,000 cubic feet per minute fan.
   d. Protection of the collected dust from moisture and other environmental hazards.
3. Installation of Equipment
4. Collection of Sample
5. Relocation of equipment from St. Louis to Los Angeles
6. Maintenance of equipment
7. Removal of equipment and site restoration

Progress

The contract has been let to the MECH-CON Corporation.

17. Project Threshold

Project Leaders Richard H. Johns and John K. Taylor

Objective

Project Threshold is a program of collaborative tests of ASTM methods for analysis of air contaminants. Begun in 1970, the project is sponsored by about 100 representatives of major industry and its trade associations. Target funding is $2.25 million for the certification of about thirty-five methods.T The NBS objective is to provide calibration materials and proceedures for ASTM.

Approach

Because of the complexities of sampling and sample storage, the approach differs considerably from that of the familiar "round robin" methods evaluation. A group of collaborators, representing from five to ten participating laboratories is brought into the field by ASTM to collect and analyze a number of samples from various point-sources. Statistical analysis of the resulting data then enables the precision and accuracy of the method to be assessed. It is the responsibility of NBS, through an ASTM Research Associateship, to provide the program with standard reference samples of the air contaminants being measured. Nine such standards have been provided to the program during 1971-73 and four additional ones are under development.

Progress

Typical air contaminants are present in the atmosphere at levels of 5-500 parts ber billion, and neither samples nor reference standards in this range are stable to storage.

In this program, primary attention has been focused on systems wherein the reference sample is generated by dilution at the point of use. One example of such a system is the permeation-tube sample generator diagrammed in Figure 17.1. This technique has reasonably broad applicability for contaminants which are liquifiable gases and possess vapor pressures of a few atmospheres at ambient temperature. Certified (SRM) permeation tubes were employed in the program for sulfur dioxide, and developmental tubes were procured from a commercial cource and used for nitrogen dioxide after calibration. Similar sources may be developed in the Threshold program for hydrogen sulfide, alkyl mercaptan, and hydrogen fluoride. As indicated in Figure 17.1, the reference materials are employed in a standard-addition or "spiking" mode. That is, the distribution manifold provides the analyst with pairs of atmospheric samples, one of which has been spiked with a known quantity of the contaminant undergoing measurement. This procedure, which is unique to the ASTM program, was conceived from a desire that the reference be exposed to the same atmospheric background as the contaminant itself.

The problems associated with simulating airborne particulate samples are legion, and a substitute procedure of "off-stream spiking" was adopted for dusts and airborne lead. By way of example, certified (SRM) Orchard Leaves was used as a lead source for spiking collected samples of airborne particulate lead. For convenience of use, these spikes were weighed into coded gelatin capsules which could be added to the collected samples during digestion. Similar encapsulated standards containing inorganic sulfate were prepared for spiking a sulfation candle procedure for total sulfur. Each of the off-stream spiking procedures was checked thoroughly in the laboratory to assure compatability with its respective method.

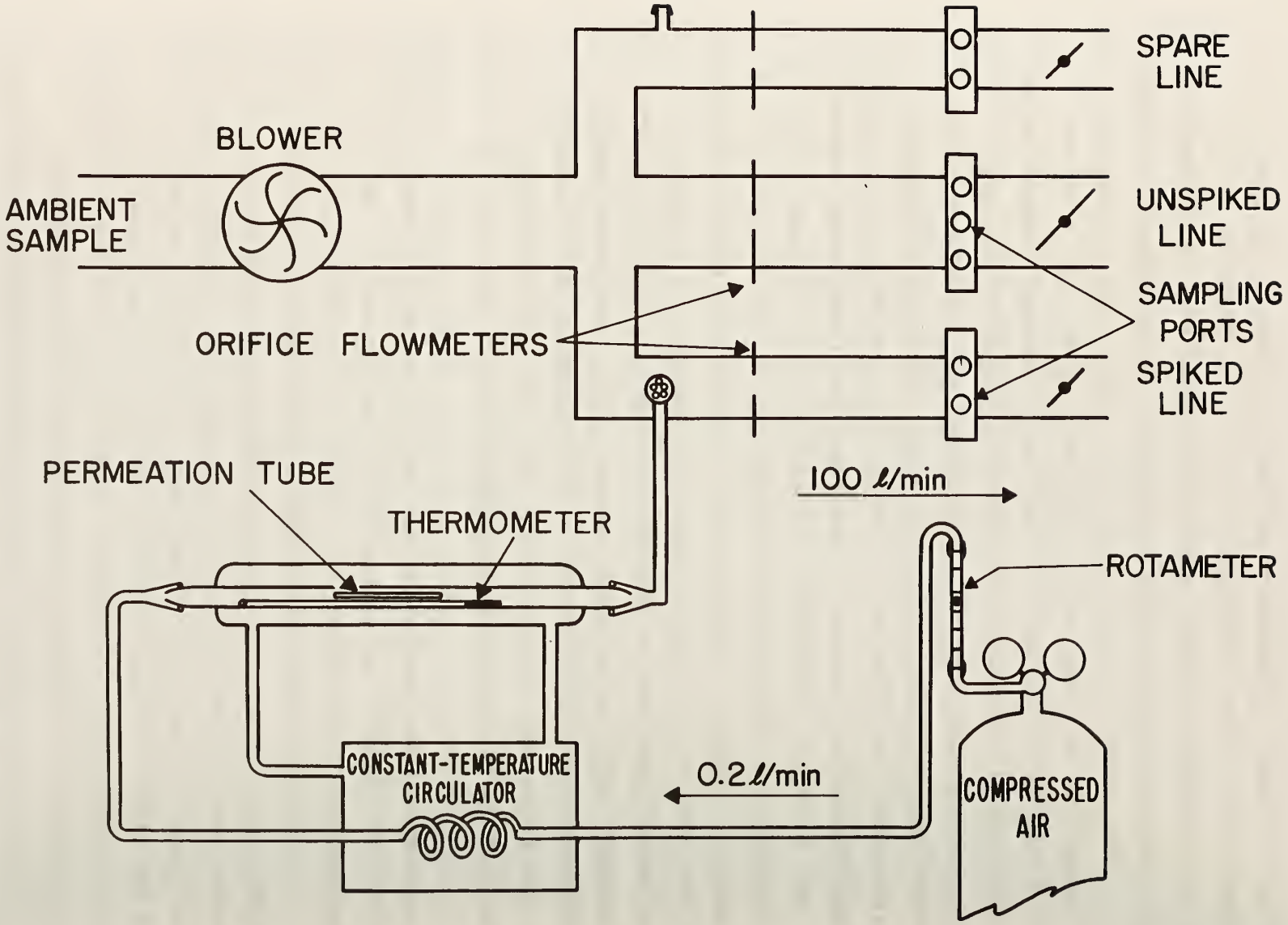


Figure 17.1 Ambient Sample Spiking System

A second group of ASTM methods is intended for the measurement of pollutants in industrial process emissions, and four of these are currently being evaluated. Several field sources were chosen which represent major emissions problems: Electric utilities, a foundry, and a cement plant. Reference materials for these methods represent quite different tasks from ambient standards, owing to concentration levels which are about 10^5 times larger than ambient for typical contaminants. Here again, the program was committed to a "spiking" or standard-addition mode of reference usage.

The spiking of an industrial facility fueled at rates measured in tons per hour is impractical. Accordingly, field Tests on such facilities were confined to the determination of repeatability and reproducibility -- the precision of the methods under test. Accuracy tests, using a spiking system developed at NBS, were conducted in a small pilot plant at Battelle Columbus Laboratories. The system is illustrated in Figure 17.2. A portion of the effluent from a furnace was piped to an adjoining laboratory via a branched line whose flow parameters could be measured accurately. To one of these lines was added a gaseous spike at a flow rate controlled by calibrated metering orifices. Previously-analyzed high purity cylinder gases (nitric oxide and sulfur dioxide) were used for the purpose. Spiking rates in these cases approached one mole per hour. Again, each collaborator was provided with sampling ports from which he could draw spiked and unspiked stack gas simultaneously. (Figure 17.3).

It is further desired to assess the precision and accuracy of the analytical procedures apart from the sampling operation. Each collaborator was supplied with triplicate ampouled samples representing three discrete levels of nitrogen and sulfur oxides. The resulting data are now being assembled

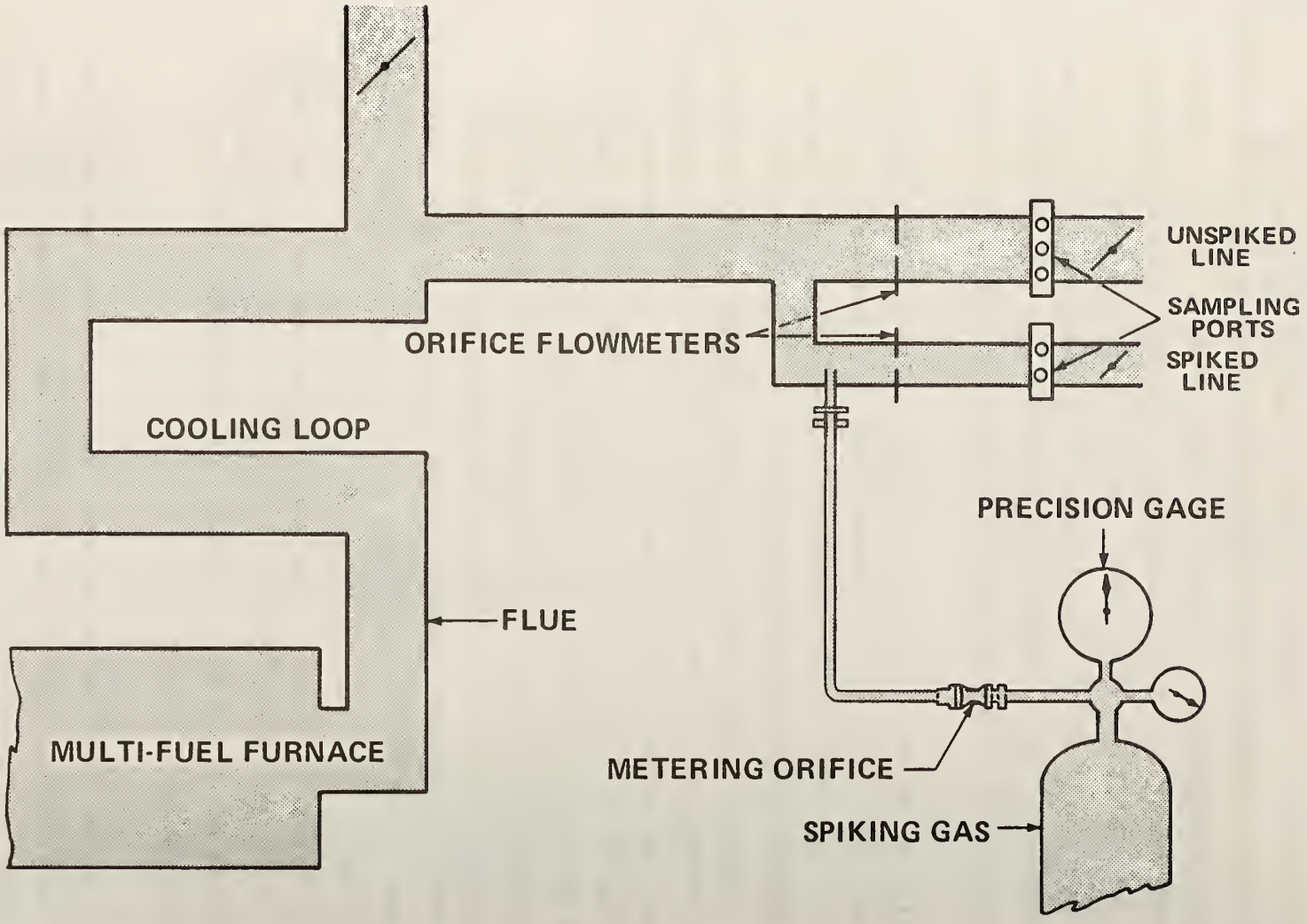


Figure 17.2 Stack Spiking System

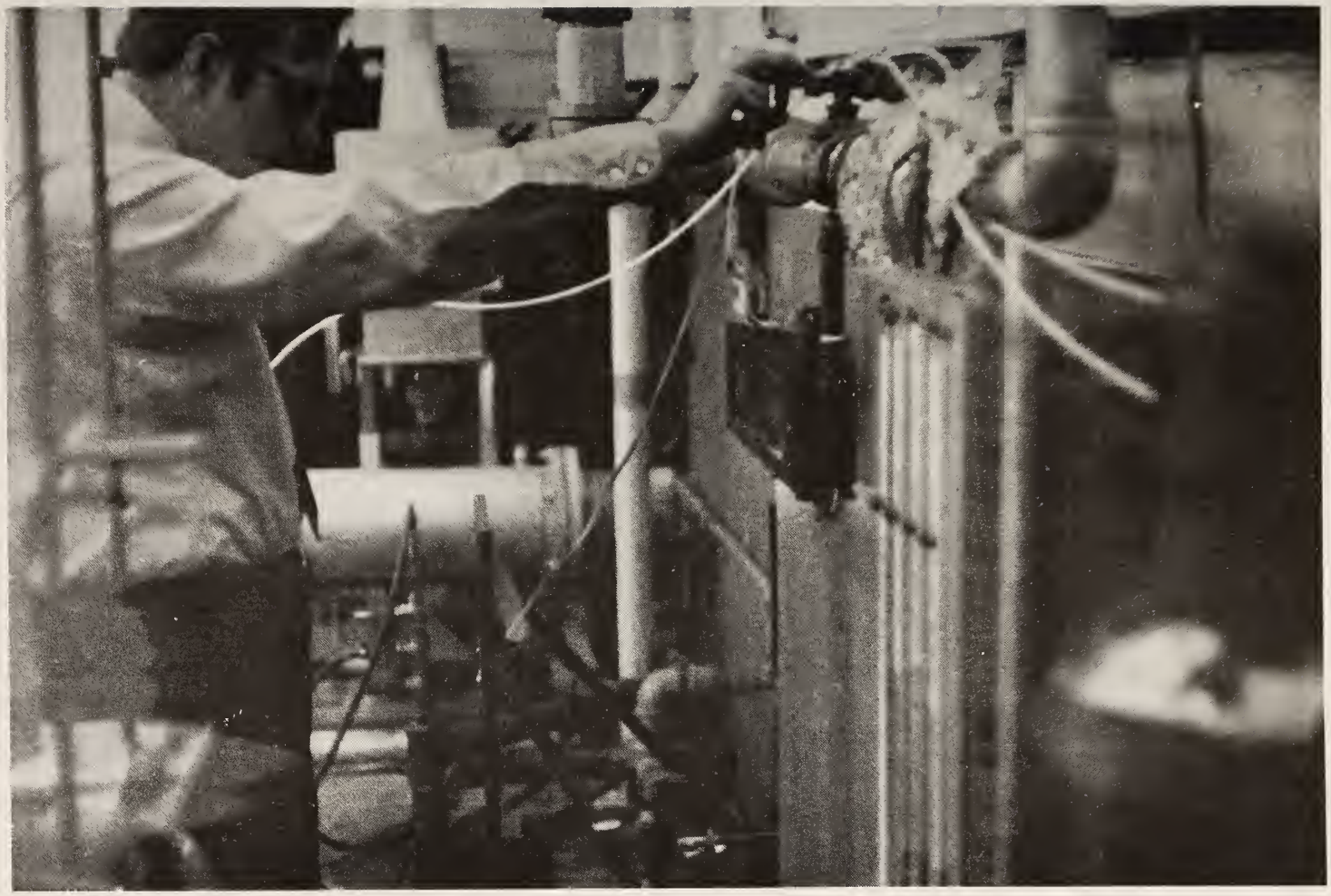


Figure 17.3 Pilot-Plant Stack-Spiking System

and analyzed to provide evaluation of the methods.

Future Work

A third phase of the program will test methods of ambient levels of fluoride, hydrogen sulfide, mercaptan and ozone. Reference materials for this purpose are under development. Permeation tube technology may provide standards for the first three of the aforementioned. A commercial ozone generator has been obtained which is capable of providing 1000 ppm ozone, to the dilution apparatus shown in Figure 17.1. This instrument has been tested for compatability with the inherent back-pressure of the system and found to be suitable for use. It will be calibrated by a chemical method at NBS before use in the field.

18. Analytical Reference Standards for Environmental Analysis

Project Leaders John K. Taylor, Ernest E. Hughes

Objective

To develop reference materials for evaluation of analytical methods applicable to industrial hygiene analysis; to develop gas-generation systems for performance evaluation of gas detector tubes and industrial atmospheric monitors. All of the reference materials are to be developed to provide maximum usefulness to the sponsor, the National Institute for Occupational Safety and Health.

Analytical test materials will be developed, specifically designed to evaluate the accuracy and precision of various optional approaches to industrial hygiene analyses. Modular gas generation systems will be designed and constructed to produce gas mixtures of known concentration. Each system shall consist of both a generator and an analytical unit to verify generation levels. For all reference standards, traceability to NBS SRM's shall be possible. In addition, the test materials shall be developed with their ultimate production as SRM's as a definite possiblity.

Progress

Generation systems have been developed and constructed to produce gaseous mixtures of 20 different substances in the concentration range 0.2 to 5.0 times the Threshold Limit Value (TLV). Table 18.1 lists the substances and the concentrations generated.

In general, the systems provide the gas mixtures at a minimum rate of 2 l/min for extended periods of time. The

accuracy of the concentration produced is at least ±5 percent and almost any concentration can be obtained, within the design limits, by adjustment of flow rates. The systems are housed in instrument cases, approximately 15 x 20 x 22 in., and are fully portable. Attempts have been made to make the systems modular, as far as possible. Thus a GDL system can be used for several purposes, with or without interchange of analytical systems.

Filter Standards

This includes reference standards for a number of substances which are normally collected in the atmosphere on filters, usually of the membrame type. Such filters are attached to a miniature pump, worn by the worker, to monitor his exposure during actual working conditions.

The analytical reference standards are not produced by collection of air-borne materials but are typical filters on which have been placed the substance of interest either from solution or suspension. While they do not simulate the collection process, they represent all of the other analytical problems and hence serve to evaluate analytical methodology.

A series of 3 filters containing lead, cadmium, zinc, and tin; a second series containing lead, zinc and manganese, and a third containing beryllium have been produced. They stradle the TLV range. The technique has been developed for producing filters on which are placed mixtures of quartz and clay, and these will be completed in the near future.

Biological Samples

A series of reference samples for clinical examination of workers has been developed. One of them consists of urine containing normal and elevated amounts of mercury, while another consists of blood containing normal and elevated concentrations of lead. Both of these were prepared in-vivo by incorporating salts of the elements into animal feedings--hogs. The concentrations were determined by intercompetence trace analysis.

Reference standards of urine containing normal and elevated levels of selenium, arsenic, copper, nickel and chromium, and a similar material containing fluoride have been produced by a spiking procedure and are now undergoing analysis. The samples will consist of freeze-dried specimens and will again serve to evaluate analytical methods.

Charcoal Tubes

Vapors such as organic solvents can be determined in the industrial atmosphere by collection on charcoal absorbers and later eluted and analyzed by gas chromatography. Techniques have been developed for producing tubes containing accurately known amounts of these solvents, and a series of them have been produced for NIOSH for use in method evaluation. The results are presently being statistically analyzed. The technique of solid-state sampling appears to be one of considerable utility, since it eliminates the need for liquid collection systems which often are a source of trouble.

Initial work has been done on iodized charcoal as a collection system for mercury vapor. Techniques have been developed to produce such tubes containing known amounts of mercury,

but production awaits a critical study of the analytical method by others.

Table 18.1

Substances and Concentrations Generated

Substances	Generation System	Analytical System	TLV in ppm	Concentration Range in ppm
Carbon Monoxide	GD	SRM	50	25 - 250
Carbon Dioxide	GD	SRM	5,000	2,500 -25,000
Ozone	UV	SP	0.1	0.05 - 0.5
Sulfur Dioxide	PT	SRM	5	2.5 - 25
Hydrogen Sulfide	PT	FP	10	5.0 - 50
Nitrogen Dioxide	PT	GV	5	2.5 - 25
Carbon Tetrachloride	GDL	GC	10	5 - 50
Tetrachlorethylene	GDL	GC	100	50 - 500
Trichloroethylene	GDL	GC	100	50 - 500
Benzene	GDL	GC	25	12.5 - 125
Ammonia	SGA-GDL	TR	50	25 - 250
Chlorine	SGA-GDL	TR	1	0.5 - 5.0
Mercury	VS-GDL	AA	0.01*	0.005* - 0.5*
Hydrogen Cyanide	SGA-GDL	ISE	10	5 - 50
Hydrogen Fluoride	SGA-GDL	ISE	3	1 - 20
Methyl Bromide	GDL	GC	20	5 - 100
Nitric Oxide	GDL	SRM	25	12.5 - 125
Methane	GDL	SRM	--	5% LEL - LEL
Arsine	SGA-GDL	SP	0.05	0.02 - 0.25
Acrolein	SGA-GDL	GC	0.1	0.05 - 5

Notes: GD = gas delivery; UV = ultraviolet; PT = permeation tube; GDL = gas dilution; SGA = stock gas analysis; VS = vapor saturation; LEL = lower explosive limit; TLV = threshold limit value; SRM = Standard Reference Material; SP = spectrophotometric; FP = flame photometric; GV = gravimetric; GC = gas chromatographic; TR = titrimetric; AA = atomic absorption; ISE = ion selective electrode.

*(mg/m^3)

19. Characteristics of Exponential Dilution Flasks

Project Leader J. J. Ritter, Inorganic Materials Division
Other Personnel N. K. Adams

Objective

Experimental examination of the capabilities and limitations of the exponential dilution flask as a certifiable device for rapid calibration of fast-response air pollution monitoring equipment.

Approach

In an ideal exponential dilution flask (EDF), a given gaseous sample is continuously diluted with a flowing carrier gas and the change of sample concentration with time is a simple first-order exponential decay process.

The decay constant (k) is related to measurable parameters in the system, viz., it is the quotient of the carrier gas flow rate and the volume of carrier gas contained within the EDF. The exponential character of this process offers a method of obtaining concentration-time information over several orders of magnitude from a single injection of sample.

The dilution technique will be tested with the EDF connected to a flame ionization detector using air as a carrier gas and propane as the sample material. The results of the exponential dilution calibration technique will be compared with those from a calibration regime utilizing a series of certified propane-air mixtures.

Progress

Our evaluation of the performance of conventionally designed EDF's led us to examine the effect of uncertainties in slope and time measurements upon the concentration values (c) calculated from the theoretical first-order equation, $c = c_o e^{-kt}$. These investigations indicated that while the time (t) could be easily measured to within 0.1 sec. slope values (k) obtained from a least-square fit of log signal vs time curves would show a standard deviation (σ) of the order of 0.02k. An evaluation of the effect of these uncertainties through an error propagation analysis[1] showed that variations in k were principally responsible for uncertainties in c. An example of this error propagation, using typical experimental values is given in table 19.1.

Table 19.1

For $k = 0.200\ min^{-1}$, $\sigma(k) = 0.02\ k$
$\sigma(t) = \frac{0.1}{60}t$, the percentage variation ($\%CV_c$) anticipated in the measurement of c is given by: $\%CV_c = 2kt$.*

t (min)	c (ppm)	$\%CV_c$
0	300	-
15	14.9	6.0
30	0.76	12.0
45	0.037	18.0

*In general, if $\sigma(t)$ is small relative to $\sigma(k)$, then $\%CV_c = \%CV_k\ (kt)$.

From this analysis it was apparent that the uncertainty in k should be reduced in order to utilize effectively the dilution technique in the calibration of air quality

monitoring instruments. The most obvious sources of uncertainty in the measured k's are related to:

1. drift in both the signal amplifications and signal integration components of the detector. (This is estimated to be in the range 0.2 - 0.4% per hour),
2. non-linearity of detector response,
3. inadequate mixing.

Flame ionization detectors are almost never truly linear. At a given flow rate, the relationship between the signal (s) and concentration (c) is given by $s = Ic^n$, where I is a proportionality constant.[8] If n = 1 the detector is truly linear. In practice n is usually found in a range between 0.95 and 0.99.

The effect of non-linearity on a measured k can be found from the following relationships:

$$s = Ic^n$$

$$c = c_o e^{-\alpha t}$$

$$\text{Thus } s = I\,(c_o e^{-\alpha t})^n$$

$$\ell n\, s = (\ell n\, I + n\, \ell n\, c_o) - n\, \alpha\, t$$

where $k = n\,\alpha$, $(\ell n\, I + n\, \ell n\, c_o)$ is a constant and $\alpha = \frac{\text{carrier flow rate}}{\text{mixing volume}}$. The expression is of the form $y = a + bx$, indicating that a plot of $\ell n\, s$ vs t should yield a straight line with $K=\alpha$ when n=1. Thus the agreement between k and α is a measure of detector linearity.

Design and performance data for EDF's are notably sparse.[2-7] There are no published critical design guidelines for EDF construction. Accordingly, as a result of our evalutation of conventional EDF's, we have undertaken to design and construct a dilution flask based on fluid dynamic

principles. (See fig. 19.1).

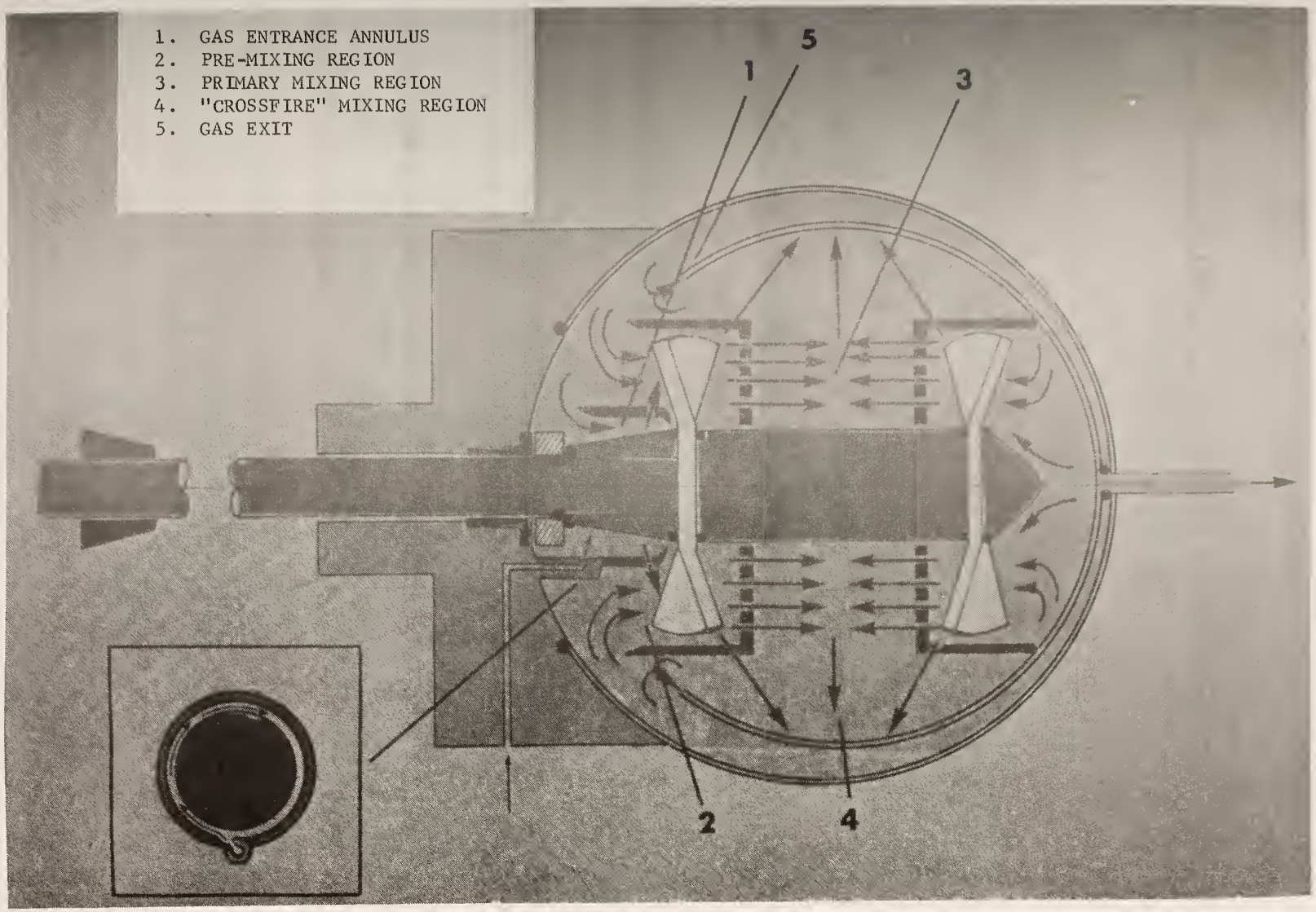
The results of the evaluation of the NBS prototype EDF are summarized below:

1. A comparatively more random distribution of residuals about the fitted lines was noted from the least-square fits.
2. Slope values (k's) obtained from runs made under essentially identical operating conditions were found to be in agreement with a standard deviation in the range 0.008 k to 0.01 k.
3. The k values, on the average, fell to within $\pm$ 1.5% of the theoretical values predicted from flow rates and mixing volume.

These results indicate that the new design approaches ideal performance more closely, and is certainly more reproducible than its predecessors. More recent experiments have been performed by introducing premixed propane-air mixtures (span gas) of accurately known concentrations and then diluting the mixtures with pure carrier gas to obtain the response curve related to all other concentrations below the span gas level. In this procedure, a change over was effected from nitrogen to air as a carrier gas which caused some perturbations in detector performance. Most of the difficulties have been resolved and preliminary indications suggest that EDF performance is comparable to that observed with the injection technique.

Our initial experiments with the EDF - flame ionization detector air-propane system indicated that the reduction of uncertainty of slope measurements to the 1% level could be readily achieved. A slope uncertainty of this magnitude will propagate an uncertainty of 4-5% in the measurement of c at the 1 ppm level under the conditions

described in Table 19.1. More recent experiments suggested that the slope uncertainty could be reduced even further to $\sigma = 0.006$ k, when careful adjustments were made of the detector fuel supply, relative to carrier gas flow rate. These results suggest that the sources of uncertainty may be as much for the detector system as for the mixing processes. Further studies oriented towards optimizing detector parameters are currently under investigation. Concurrently, an independent survey of detector linearity using Standards Reference Materials is in progress as well as a study designed to suggest the best operational technique in using an EDF to calibrate a flame ionization detector.


1. GAS ENTRANCE ANNULUS
2. PRE-MIXING REGION
3. PRIMARY MIXING REGION
4. "CROSSFIRE" MIXING REGION
5. GAS EXIT
1
5
3
2
4

References

1. J. Mandel, The Statistical Analysis of Experimental Data, Interscience Publishers, New York (1964) p.72

2. J. E. Lovelock, Gas Chromatography, R. P. E. Scott ed., Butterworths, Inc. Wash. D. C. (1960).

3. J. E. Lovelock, Anal. Chem. 33, 162, (1962).

4. H. P. Williams, and J.D. Winefordner, J. Gas Chrom., 4, 271, (1966).

5. G. Greco Jr., F. Gioia, F. Alfani, La. Chimica EL'Industria, 53, 1133, (1971)

6. Arthur Fontijon, Alberto Isabadell, and Richard J. Ronco, Anal. Chem. 42, 575, (1970)

7. J. Krugers, Instrumentation in Gas Chromatography, J. Krugers ed., Centrex Pub. Co. Eindhoven, Netherlands (1968) p. 24

8. H. M. McNair and E. J. Bonelli, Basic Gas Chromatography 5th ed., Varian Aerograph Inc. California, (1969), p. 88

20. Calibration Standards by Thermal Decomposition

Project Leader Wing Tsang, Physical Chemistry Division
Other Personnel Douglas Cornell, on Leave From Fairleigh-Dickenson University

Objective

The aim of this project is to investigate the possibility of generating dilute, known quantities of pollutant gases through the thermal decomposition of appropriate "parent" compounds. Such an *in situ* procedure provides a simple solution to the difficult problem of preserving the integrity of dilute samples of pollutant gases prepared in the usual static manner. Futhermore, through the proper selection of the parent molecule, such a procedure may be easily calibrated. That is, for the reaction A (parent)→B (pollutant)+ C, where C is a more stable and easily calibratable species, then a determination of the concentration of C will fix the value for B. Finally, by controlling the concentration of the "parent" molecule and/or the extent of decomposition, any concentration of pollutant can be readily produced. Overall, the present procedure calls for a minimal amount of experimental skill and is thus ideal for incorporation into test instruments and routine field usage.

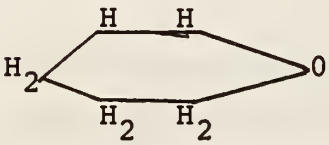
The experimental procedure is to use as the parent compound a molecule which decomposes into the desired components via a molecular mechanism. It is particularly important that there is no possibility of free radical induced decomposition since such systems may not be reproducible. The selected compound is then pyrolyzed in a gold tube reactor (flow rate ~20 cc/min, residence time ~ 6 sec) and the requirements are that only the expected products

be produced and in the proper stoichiometric proportions. The extent of decomposition is varied from <1% to 100% and is determined by the temperature of the reactor. Sample introduction is either by liquid injection (dilute quantities of parent compound in toluene) or by flowing the helium carrier gas over a sample (liquid or solid) of the parent compound and thus introducting a mixture that is related to the vapor pressure of the compound. The experimental set up is seen in Figure 20.1. By suitable changes in connections it is also possible to generated the desired pollutant continuously. Detection may be by gas chromatography with flame and helium ionization detection. In the case of SO_2 and NO it proved to be necessary to use the fluorescence detector of Okabe (Project No. 3).

During the first half of the present year, a demonstration of the feasibility of this method as a means of generating formaldehyde, acetaldehyde and acrolein has been completed. The relevant reactions are

$$H_2C{=}C(CH_3){-}CH_2CH_2OH \longrightarrow \text{isobutene} + HCHO$$

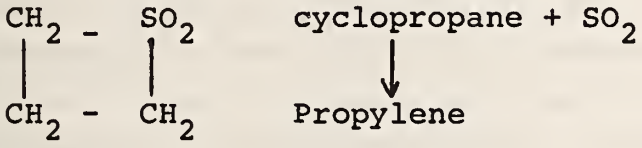
$$H_2C{=}CH{-}CH_2CH(OH)CH_3 \longrightarrow \text{propylene} + CH_3CHO$$

and  $\longrightarrow$ ethylene + $H_2C{=}CHCHO$ (acrolein)

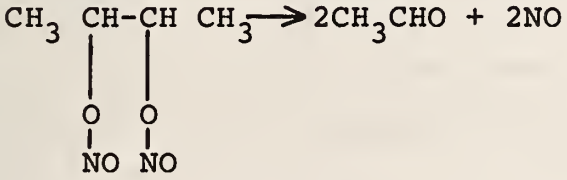
Quantitative results are summarized in Figures 20.2,20.3, a and 20.4. The key points to be noted are the equality (on a mole basis) of the olefins and aldephydes formed, the great variation in the concentration delivered to the

detector and the wide range of temperatures employed (entered parentheticitly in the figures). The latter demonstrate that temperature control is not critical for the present application. On the basis of these results it is suspected that the generation of organic acids, alchols, ketones and hydrogen halides will proceed with equal facility. A paper on these matters has been prepared and submitted for publication.

Two substances that appear to behave in the required manner for generation of SO_2 and NO are shown in the following reactions.



and



It has been demonstrated with trimethylenesulfurdiodixe that proportional amounts of C_3H_6 (cyclopropane plus propylene) and SO_2 are formed over all reaction conditions. This is also the case for acetaldehyde and NO except at high extents of decomposition where CH_3CHO may well be quenching NO fluorescence. There remains the need of absolute calibration of the SO_2 and NO fluorescence signals. This will permit plots similar to those given in Figures 20.2, 20.3, and 20.4.

It should be noted that the trimethylene sulfur dioxide system has characteristics which make it ideal for present

applications. For example, at 0°C it is a solid with a vapor pressure of the order of 0.03 Pa (0.2 microns). Thus, with a carrier gas at 1 atm and with complete reactions (>800°K) one obtains SO_2 at the .3 ppm level. At 70°C it is a liquid and its vapor pressure is such that with 1 atm of the carrier gas one obtains ~300 ppm samples. (Note that as long as saturation is maintained the concentration is independent of flowrate.) Futhermore, the extent of cyclopropane conversion to propylene provides an excellent internal check with regard to the temperature of the pyrolyzer.

In the coming year we hope to complete our work on the SO_2 system. This includes calibration with a permeation tube and the use of a stainless steel pyrolyzer. With regard to the dinitrite, aside from the absolute calibration we hope to investigate the pyrolytic properties of several other dinitrites. The aim is to obtain some internal standard other than acetaldehyde and also to find parent substances which have a lower vapor pressure than the nitrite used here. We also hope to begin work on a pyrolytic source for CO.

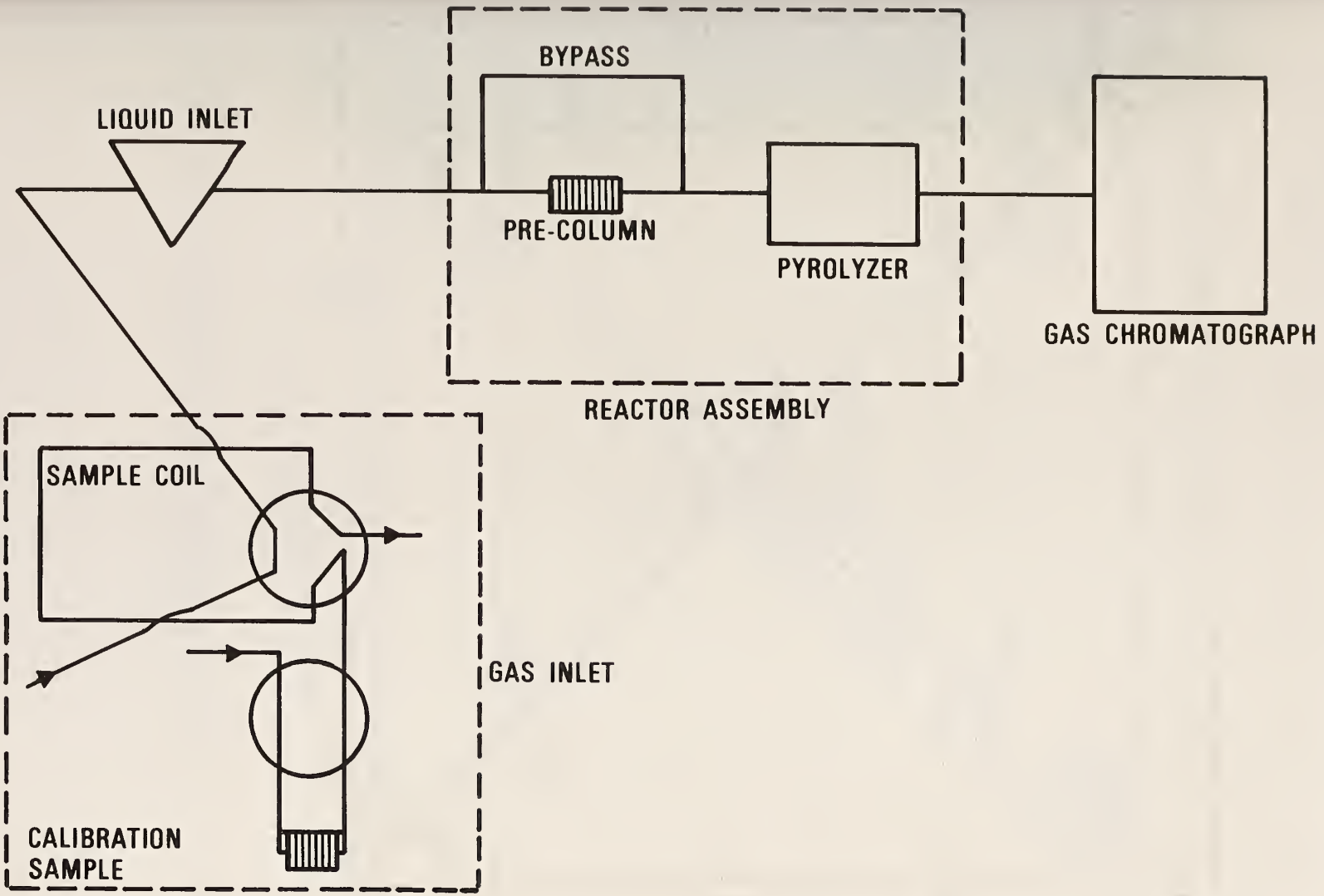


Figure 20.1 Experimental Set-up

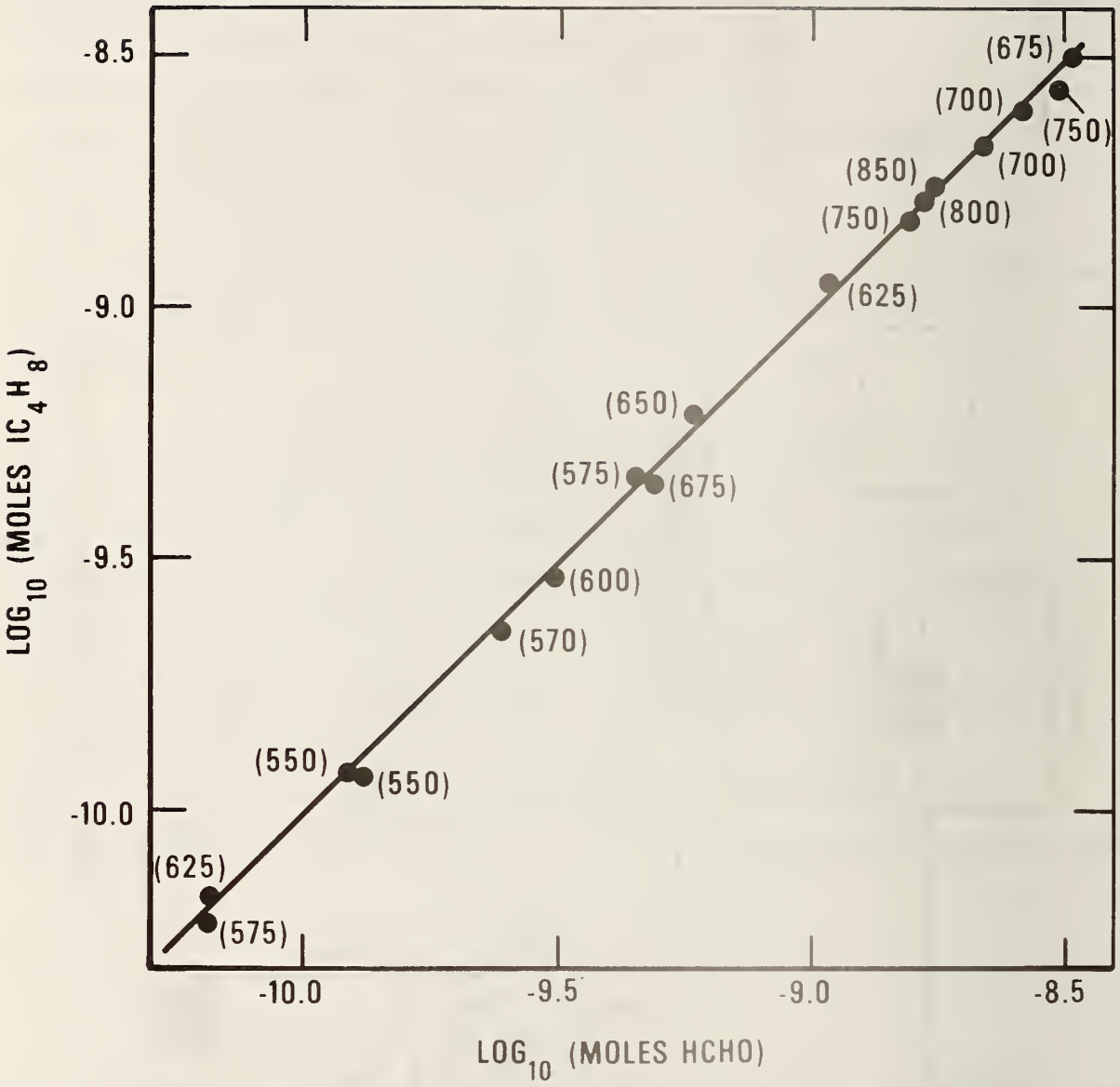


Figure 20.2 Yield of aldehyde as a function of olefin and reactor temperature ()

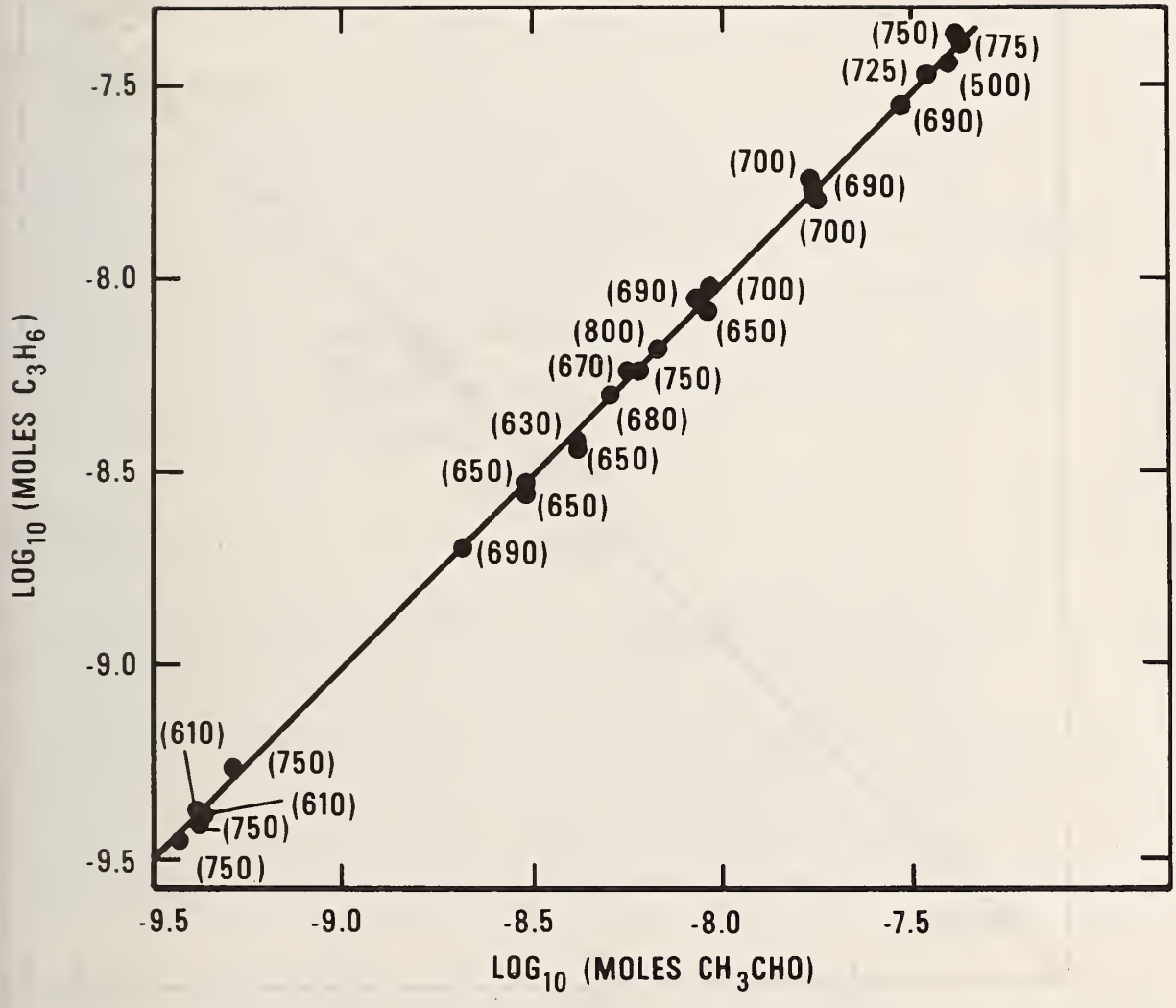


Figure 20.3 Yield of aldehyde as a function of olefin and reactor temperature () K

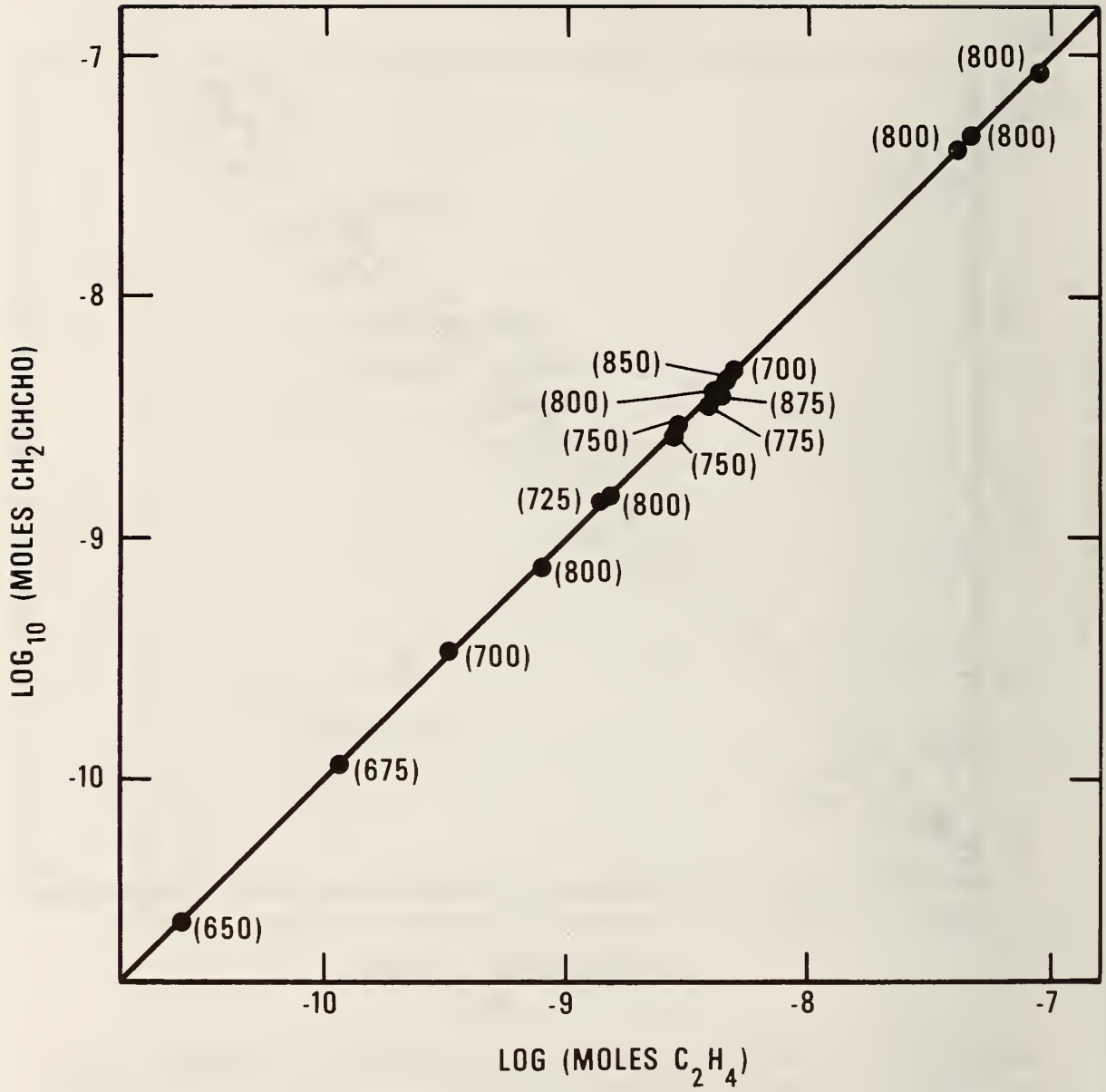


Figure 20.4 Yield of aldehyde as a function of olefin and reactor temperature () K

21. Gas Dilution System

Project Leader F. W. Ruegg, Mechanics Division
Other Personnel G. P. Baumgarten

Objective

The project is to provide a prototype gas proportioning system. The system is to mix a concentrated pollutant-in-air with pure air in the necessary proportions to produce three specific low concentrations by which monitoring instruments can be checked for errors in analysis. Simplicity and practicality rather than high accuracy are overriding considerations for the Sponsor, EPA.

Approach

The system proposed is composed of two types of metering devices. A critical flow nozzle is to be used to meter the pure diluent air and laminar flow devices to meter the concentrated pollutant. The two flows will be brought together in a mixing section and delivered to an outlet connection. Both capillary tubes and porous plugs are under consideration as the laminar flow devices.

Progress

Six critical flow nozzles have been fabricated and are being flow tested for reproducibility of construction. Three sizes of porous plugs and a flame photometric sulfur dioxide analyzer were loaned to us by EPA to compare the performance of the porous plugs vs. capillary tubes, and to evaluate the accuracy of the prototype delivery system. A small positive displacement prover has been

built to measure and calibrate the very low flows needed from the laminar flow devices. In preliminary use of the small prover it appears to perform satisfactorily.

22. Automotive Exhaust Flowrate Measurement

Project Leader F. W. Ruegg, Mechanics Division
Other Personnel J. E. Potzick

Objective

Develop and evaluate a real-time, essentially non-instrusive, mass rate-of-flow meter for use in measurement of automotive pollutant emissions. Measurement uncertainty reduction to one percent is the goal.

Approach

Survey devices and principles applicable to flowrate measurement of automotive exhaust. Perform trial experiments toward selection of a method and/or devices for development which show promise for real-time, non-intrusive mass-rate of-flow measurement of the unsteady flow of exhaust gas.

Progress (February to June 1973)

A survey of the literature and of commercial instruments has been made for selection of methods and or devices for trial. Sonic and ultrasonic methods of flow measurement appear to offer the most promise for development. Rather intensive development and application of these principles is evident in the U.S., but all developments appear directed to measurement of volume rather than mass-rate-of-flow.

Two approaches toward measurement of mass rate have been selected for initial experiments hopefully designed to determine the most promising approach. Method 1 involves use of sonic pulses, generated by a spark or other means,

and determination of the difference in flight time to upstream and downstream pulse sensors. Method 2 involves use of high frequency (40 k Hz) continuous sound waves, and determination of their phase difference at sensors upstream and downstream from the wave source. Phase difference can be expressed as a time difference Δt, and both methods can give the mass-rate-of-flow per unit area, ρV as

$$\rho V = \left(1 - \frac{n + 1}{2n + 1}\right) \left[\frac{kp}{L} \left(1 - \frac{V^2}{c^2}\right)\right] \Delta t.$$

The quantity in [ ] is expected to be little changed by flowrate and gas composition over the range of use and hopefully can be determined as a part of the calibration factor. The quantity n defines the velocity profile in steady, turbulent flow in round pipe, and must also be determined by calibration, especially in the situation of unsteady flow in the auto exhaust tail-pipe.

Pressure p at the auto tail-pipe will not undergo large excursions and therefore is included in the bracketed term [ ]. Flowrate information in digital form and as a function of the time can be secured with method 1. Method 2 probably cannot follow high frequency changes in flowrate due to time delays in the electronic apparatus. Some very preliminary trials of method 1 indicate further trials should be made, and electronic apparatus is being assembled. Meanwhile other apparatus is being assembled for calibration of the sonic and ultrasonic meters under development. This includes both a shock tube for response-time calibrations and a steady flow air system with some heat input for steady state, but variable density, calibrations.

Further consideration was given to use of a commercial cooled sensor for mass flow measurement. Consideration of the fouling problem (frequent calibration requirement)

and the difficulty in specifying its performance in rapidly changing gas temperatures made it appear too unattractive for investigation at this time.

A commercial ion deflection mass meter has been tested over the density and flow range of interest. Although its performance could be adequate with dry air, its sensitivity to fouling and gas composition changes probably precludes its development into an effective exhaust gas meter. Further tests are planned of its response time and of its sensitivity to exhaust gas composition changes.

23. Survey of Various Approaches to the Chemical Analysis of Environmentally Important Materials

Project Leaders - B. Griefer and J. K. Taylor, Analytical Chemistry Division

Other Personnel D. A. Becker, P. J. Paulsen, S. D. Rasberry, K. F. J. Heinrich, T. C. Rains, R. W. Burke, D. W. Golightly, E. J. Maienthal, R. A. Durst

Objective

To evaluate various approaches to the chemical analysis of heavy industry process materials and waste products for constitutents that may find their way into the environment and be considered pollutants, on a cost-benefit basis.

Approach

A literature survey, together with the experience of analytical experts at NBS was used to assess the capability and cost of analysis for environmentally important materials.

Progress

A cost-benefit study has been made of a number of analytical techniques on the basis of the following performance parameters: Instrumentation requirement; detection limit; accuracy; sample preparation; sample size; manpower skills; cost per analysis.

The capabilities and costs of nuclear methods, spark source mass spectrometry, x-ray fluorescence and electron microprobe spectrometry, atomic absorption spectrometry, absorption spectrophotometry, atomic emission spectroscopy, voltammetry (polarography) and potentiometry (ion-selective electrodes)

for determining traces (less than 100 parts per million) of mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver, tin, iron, strontium, sodium, potassium, calcium, silicon, magnesium, uranium, and thorium in such matrices as fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes have been assessed.

A comprehensive report has been prepared with a chapter devoted to a discussion of each analytical technique. A general discussion is given of the problem of trace analysis in environmental studies, including material balance considerations.

Extensive use is made of tabular formats in the presentation of the data. The report includes a critically selected bibliography of the current literature on environmental trace analysis.

24. Electron Spectroscopy For Gas Analysis

Project Leader C. E. Kuyatt, Optical Physics Division
Other Personnel R. Celotta, S. R. Mielczarek

Objective

To determine the applicability of electron energy loss spectroscopy to gas phase quantitative analysis, to assess the sensitivity of the procedure and to improve the ultimate sensitivity and reliability of the method.

Approach

The NBS Model AN electron spectrometer, shown in Fig.24.1 was the analytical instrument. The electron gun is a Pierce type diode run in the temperature limited emission region of its cathode, a Philips dispenser cathode, type A. A three lens system, containing two sets of four quadrant deflection plates, injects the electrons into a monochromator which is noramlly operated at a center potential of 11 volts and a $E/\Delta E$ of 1000.

The electrons are then accelerated and deflected by three more lenses and two more sets of deflectors, until they pass through a 0.003" entrance aperature to the gas scattering cell with an energy of 100 eV and an energy dispersion of approximately 25 meV FWHM. Losses in electron energy occur as a result of interaction of a electrons with molecular species, raising the gas to discrete energy levels above the ground state.

The electrons leave through a 0.012" aperture, are decelerated to 3 volts and analyzed with a $E/\Delta E$ of 100. The magnitude of the decelerating voltage determines the value

of the energy loss to be observed. Finally, the electrons are accelerated again and the beam is focused on the cathode of a multistage electron multiplier.

The path length inside the gas scattering cell is 1.5 mm and the angular acceptance of analyzer injection optics is limited to a solid angle of 0.02 steradians. Typically, an electron current of 10^{-8} amp is utlized.

Progress

The following gases and nominal concentrations in helium were studied: acetone (100 ppm), n-hexane (100 ppm), ethanol (100 ppm), benzene (10 ppm) and trichloroethylene (10 ppm). These mixtures were produced by the Matheson Company and analyzed by Matheson to a stated accuracy of $\pm$ 5% by means of gas chromatography. Additionally, a mixture of all five of the above trace contaminants in helium had been supplied by Matheson and analyzed to the same accuracy.

Mixtures of CO in dry air (20% O_2, 79% N_2, 0.9% Ar, 0.1% CO_2) were studied at nominal concentrations of 10, 50 and 200 ppm. This was repeated with water saturated air. These gases have been prepared and analyzed by the Analytical Chemistry Division of NBS. The CO concentration is accurate to $\pm$ 2%.

Also analyzed were mixtures of N_2O (50 ppm) in N_2 and CH_4 (50 ppm) in O_2. These have been prepared by Matheson and analyzed to a stated accuracy of $\pm$ 5%.

In the analysis of gaseous mixtures, the spectrum of the mixture is fit by the method of least squares to the spectra

of the separate pure substances. From this least squares fit, the concentration of each individual component of the mixture is determined. Comparison of these determined concentrations with those concentrations provided by the gas blend supplier indicated that the analysis technique is working well (although there is as yet some unexplained difficulty with ethanol.) The fact that there are no run-to-run variations in the relative intensity across the spectrum of a particular substance or mixture indicates that the "up-down" energy sweep procedure leads to the cancellation of long-term, linear intensity drifts. The accuracy of the determined concentrations as compared to the "known" concentration also indicates that square root of mass correction for differential effusion from the scattering chamber is sufficiently accurate.

Difficulties are still encountered in the determination of the concentrations of two substances when the concentrations of these two substances differ by several orders of magnitude. Small errors in the line shape of the concentrated substance can lead to substantial errors in the determined concentration of the dilute substance when the spectra of the two substances overlap.

Work is also planned on providing techniques for adjusting line shapes at varying energy resolution to correspond to some standard energy resolution.

Our work with methane in oxygen has pointed out the importance of low, or at least structureless, background signals. We have completely disassembled and cleaned the instrument in order to lower the background.

A major problem in the accumulation of data during the course of these experiments has been the lack of a readout

device for observing the data during, or soon after, the experiment. A problem, such as the existence of a background, might not be noticed until a few days later. To remedy this situation we have designed and constructed a cathode ray tube display system, which, when used with mini-- computer, provides a real time display of our data.

An experiment can benefit from more signal and less background noise, and to this end we shall attempt to improve the electron spectrometer by a careful redesign of the electron optics. This redesign is facilitated by the use of a computer optimization procedure for electron lens design which has recently been developed by Kuyatt and applied successfully at NBS.

Finally, a great deal of effort was expended during the past year in developing procedures to accumulate, store, process and analyze large quantities of data. We were careful to make these systems flexible and fairly easy to modify. Now that the ground work has been done, we plan to test different techniques of data accumulation and analysis toward the goal of greater sensitivity and reliability for electron energy loss spectroscopy as an analytical tool.

25. Laser Magnetic Resonance Spectroscopy

Project Leader K. M. Evenson, Quantum Electronics Division
Other Personnel C. J. Howard, NOAA Aeronomy Laboratory

Objective

Develop Laser Magnetic Resonance Spectroscopy for the purpose of measuring concentrations of free radicals of interest in tropospheric and stratospheric pollution.

Approach

Rotational levels of paramagnetic molecules can be Zeeman shifted into coincidence with far infrared laser lines to produce resonance absorption of laser radiation. This technique, called laser magnetic resonance, was first demonstrated with O_2[1,2,3] and has subsequently been successfully applied to other stable molecules such as NO[4] and NO_2[5]. Recently, the Zeeman rotational spectra of the transient free radicals OH[6,7] CH[8], HO_2[9], and HCO[10] have also been observed.

The laser magnetic resonance (LMR) spectrometer used in most of these studies is shown schematically in Fig. 25.1. The laser oscillates in the cavity between mirrors C and D in a single longitudinal mode. The cavity is divided into two parts by a dielectric beam splitter; the sample or absorption region is on the left and the active laser medium, a dc discharge, is on the right. The beam splitter serves three purposes: (1) it provides a vacuum seal between the absorption cell and the laser discharge, (2) it acts as a reflector to couple a small fraction of laser power out of the cavity to detectors A and B (for this purpose

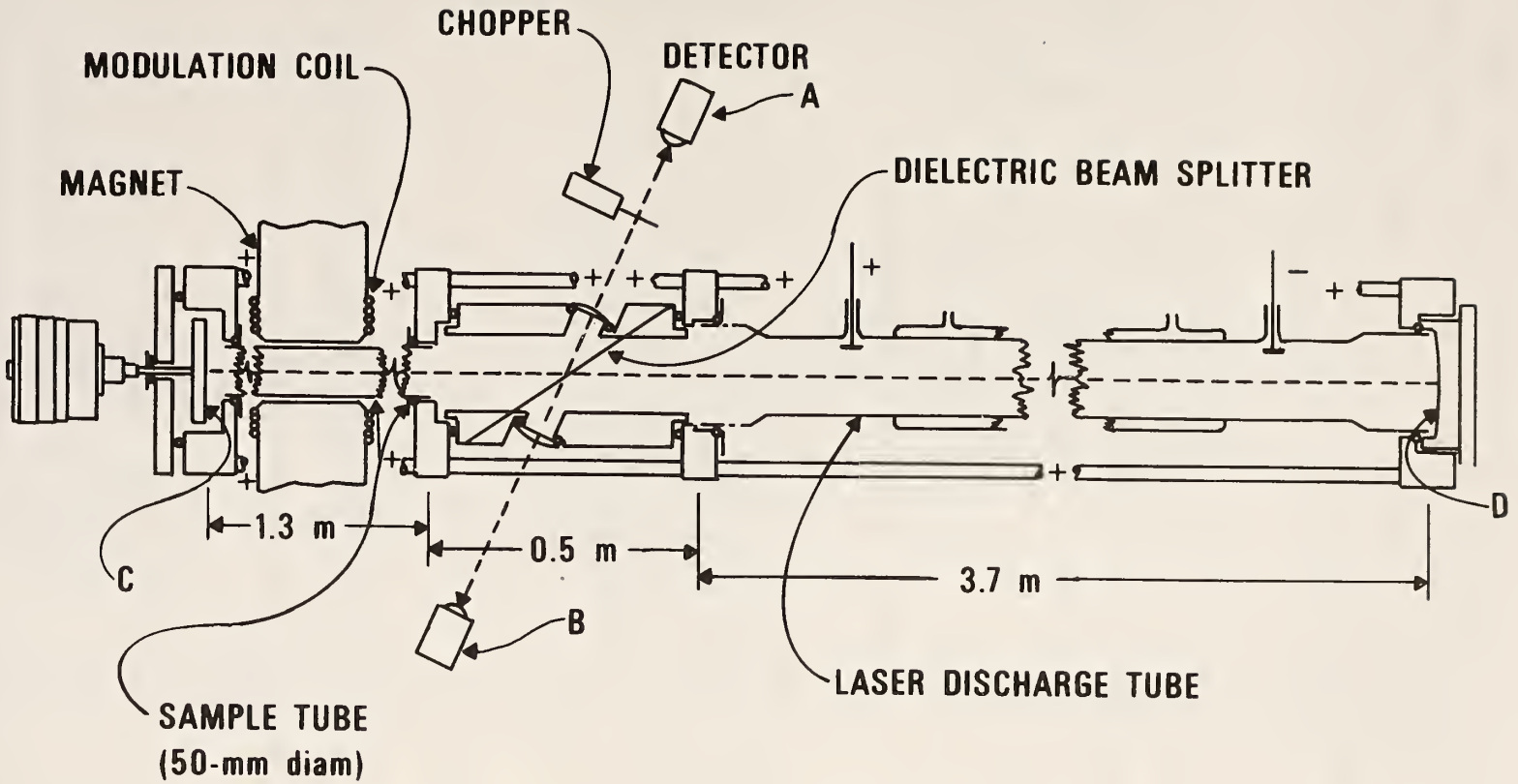


Figure 25.1 Schematic diagram of the LMR apparatus.

its angle with respect to the axis of the laser is adjustable near the Brewster angle), and (3) it restricts the laser radiation to a single linear polarization which may be oriented either parallel or perpendicular with respect to the magnetic field in the absorption cell.

Dectector A is a Golay cell which is normally used for tuning the laser to the desired wavelength and power level. The laser can be operated at 78, 79, or 119 μm with H_2O vapor in the discharge tube and at 72, 84, or 108 μm with D_2O. The power level is normally between 1 and 10 μW at the detectors. Detector B is a liquid helium cooled Bolometer which is used to detect the modulated absorption signal during spectroscopic measurements.

A 15 inch magnet with 5.5 inch ring shimmed pole tips and a 2 inch air gap was used to produce fields up to 23.5 kG in the absorption cell. An adjustable field modulation of up to 100 G at 270 Hz was used to generate the modulated absorption signal which was measured using phase sensitive detection.

Progress

Figure 25.2 shows an HO_2 spectrum taken with the 79 μm water vapor laser line. In this case the electric field of the laser radiation was polarized parallel to the dc magnetic field.

The high sensitivity and versatility of the laser magnetic resonance spectrometer has made it desirable to combine it with a flow reaction system for the study of free-radical reaction kinetics. Measurements are now being made on several important reactions, of OH, HO_2, and CHO. This is the first time it has been possible to study directly

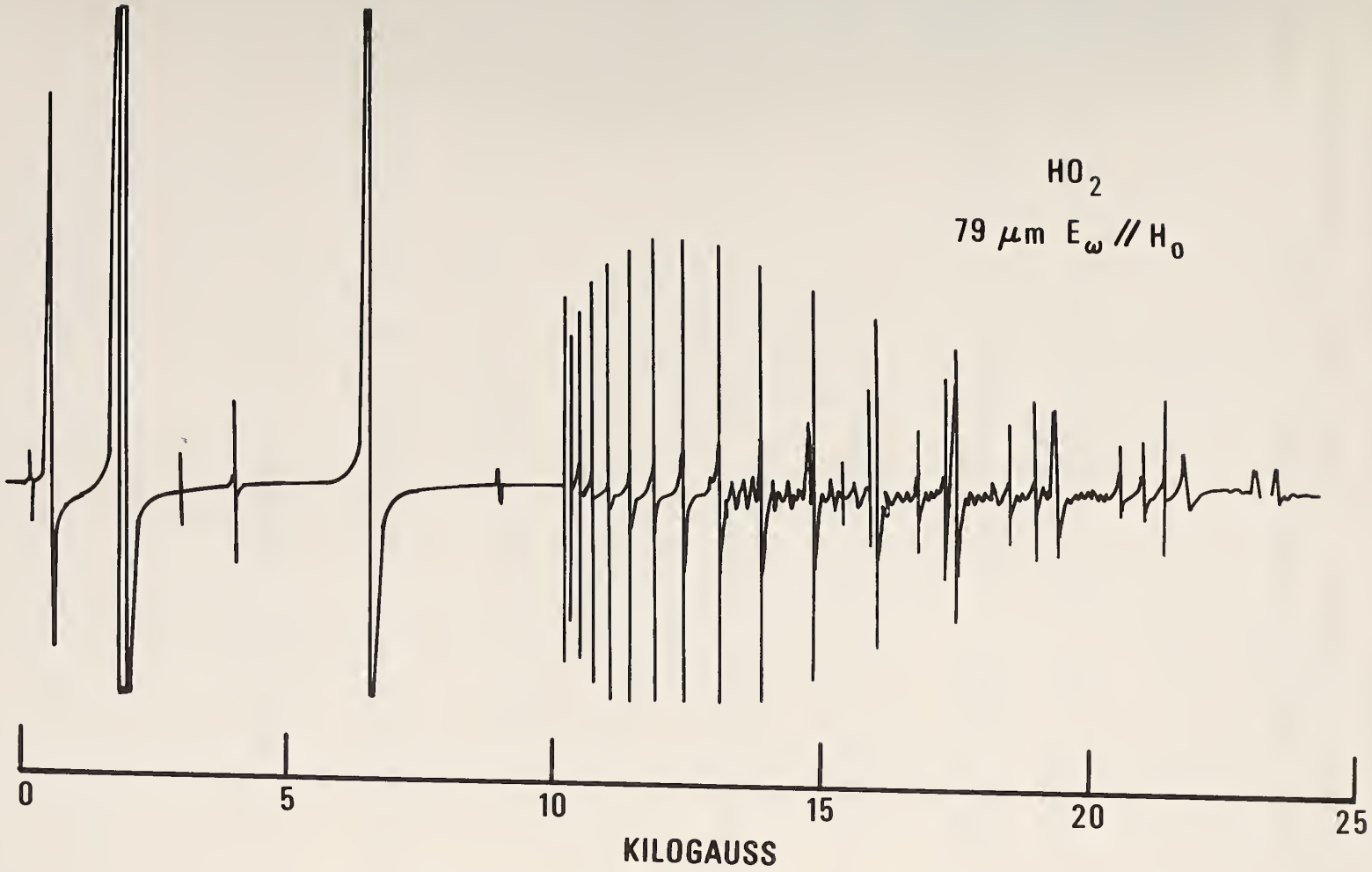


Figure 25.2 HO_2 spectrum - 79μm line of H_20 laser with laser electric field parallel to the dc magnetic field.

the kinetics and mechanisms of numerous radical reactions which are necessary for a complete understanding of the chemistry of discharges, flames and other combustion processes, and of the atmosphere.

References

1. K. M. Evenson, H. P. Broida, J. S. Wells, R. J. Mahler, and M. Mizushima, Phys. Rev. Letter 21, 1038 (1968)

2. M. Mizushima, J. S. Wells, K. M. Evenson, and William M. Welch, Phys. Rev. Lett. 29,831 (1972)

3. K. M. Evenson and M. Mizushima, Phys. Rev. A6, 2197 (1972)

4. M. Mizushima, K. M. Evenson, and J. S. Wells, Phys. Rev. A5, 2276 (1972).

5. R. F. Curl, Jr., K. M. Evenson, and J. S. Wells, J. Chem. Phys. 56, 5143 (1972).

6. K. M. Evenson, J. S. Wells, and H. E. Radford, Phys. Rev. Lett. 25, 199 (1970)

7. P. Kasuya and K. Shimoda, Japan J. Appl. Phys. 11, 1571 (1972).

8. K. M. Evenson, H. E. Radford, and M. M. Moran, Jr., Appl. Phys. Letter. 13, 426 (1971).

9. H. E. Radford, K. M. Evenson, and C. J. Howard [Paper in preparation].

10. R. F. Curl, Jr., C. J. Howard,and K. M. Evenson (Paper in preparation).

26. Kinetics of Atmospheric Reactions

Project Leader W. Braun, Physical Chemistry Division
Other Personnel M. J. Kurylo, A. Kaldor

Objective

Measure kinetics of reactions of importance in assessing the perturbation of stratospheric chemistry by future SST traffic. The studies are being conducted as part of the Climatic Impact Assessment Program of the Department of Transportation.

Approach

The method of flash photolysis resonance fluorescence is used. The apparatus was designed to permit kinetic investigations of systems containing such reactive species as NO_2 and O_3. In addition, it encompasses a facility for monitoring such species by light absorption techniques during the course of a chemical reaction. The working system was optimized for atom detection and then modified for the study of OH radical chemical dynamics.

Progress

The all-glass variable temperature cell, which is well suited for the atomic studies, gave too much light scattering to be suited for OH investigations. Consequently, the stainless steel outer chamber was Teflon coated and used for some room temperature OH measurements. A larger stainless steel variable temperature cell (more accessible for internal light collimation) is currently being constructed.

The reaction $OH + NH_3 \rightarrow H_2O + NH_2$ was investigated at 298K. A rate constant of 4.1×10^{14} cm^3 $molec^{-1}$ s^{-1} was obtained. Through a comparison of a number of OH and O atom reactions involving NH_3, CH_4, and C_2H_6 a lower limit for the rate constant at stratospheric temperature (225K) was calculated. This calculation indicates that the reaction of OH with NH_3 becomes the rate determining step in the conversion of NH_3 into NO_x via reaction of NH_2 with O_2 and O_3.

A mixing ratio of 10^{-9} for stratospheric NH_3 is thereby capable of introducing as much NO into the stratosphere as does the reaction of $O(^1D)$ with N_2O. This latter reaction is presently considered as the dominant natural production mechanism for NO in the stratosphere. The possibility of a larger natural source can minimize the significance of any artifical input of NO_x(i.e., SST engine exhaust).

The reaction $OH + O_3 \rightarrow HO_2 + O_2$, an important step in the photochemistry of wet ozone, was studied at 298K. The rate constant of 6.5×10^{-14} cm^3 $molec^{-1}$ s^{-1} confirms the most recently measured values of other workers. As such, it tends to indicate the validity of these workers' low temperature results, thereby minimizing the importance of the reaction as a part of the destructive mechanism for stratospheric ozone.

It is planned to extend the studies of the $OH + NH_3$ and $OH + O_3$ reactions to conditions of stratospheric importance. Future OH radical investigations will also include the $OH + SO_2$ reaction. The atomic systems to be investigated will include reactions in the chlorineoxygen system (i.e. $Cl + O_3$, $Cl + O_2 + M$, etc.). Such reactions may bear on atmospheric perturbations caused by space shuttles.

Complementary to our atmospheric kinetics program, an investigation of the influence of laser excitation on chemical reactivity was begun during the past year. A large number of atom-molecule and molecule-molecule systems were studied in a preliminary way. To date, the NO + O_3 reaction has yielded the most promising results. The absorption of 9.6μ radiation from a CO_2 laser by O_3 has a definite enhancement effect on the reaction rate. The study of this and other O_3 reactions (viz with Cl and O) will be studied during the coming year. These experiments are being conducted in collaboration with the newly formed Laser Program at NBS headed by Dr. DesLattes.

27. Atomic Reaction Kinetics

Project Leaders J. T. Herron and R. E. Huie, Physical Chemistry Division

Objective

The objective of this project is the kinetic characterization of the elementary reactions which may play an important role in troposperic and stratospheric air pollution chemistry. Specifically, this includes the reactions of atomic oxygen, singlet molecular oxygen, ozone and hydroxyl radicals with primary organic pollutants, and with the oxides of nitrogen and sulfur.

Approach

The approach used is a combination of laboratory studies with data compilation and evaluation.

The laboratory programs center around the NBS chemical kinetics mass spectrometer, used for the study of atomic oxygen, singlet molecular oxygen and ozone chemistry, and the resonance fluorescence facilities at NBS and at the University of Maryland used for the study of atomic oxygen reactions.

In the case of the atomic oxygen reactions, the laboratory program is designed to complement the data evaluation program by establishing absolute rate constants for key reactions to be used in converting the existing large body of relative rate measurements into absolute rate constants, and to provide data on important reactions where none exists or where the existing data are unreliable.

Progress

The principal accomplishments in FY 1973 have been in the measurement and evaluation of atomic oxygen rate constants.

Rate constants for the reactions of atomic oxygen with O_2 and NO_2 have been measured over a wide range of temperatures. The rate constants are:

$$k_{O_2} = 6.57 \pm 0.59 \times 10^{-35} \exp(1014 \pm 46/RT) \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$$

$$k_{NO_2} = 9.12 \pm 0.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ from } 230\text{-}339\text{K}.$$

These reactions play a critical role in determining the ozone profile in the stratosphere. This work was supported in part by DOT under the CIAP program which attempts to assess the importance of exhausts from stratospheric aircraft flights on the concentrations of ozone.

Rate measurements of interest to tropospheric air pollution have also been carried out. Rate constants for the reactions of atomic oxygen with ethylene, the butenes, tetramethylethylene and some haloethylenes have been measured. In addition studies on the oxidation of SO have been initiated from the point of view of the origin and control of SO_2 in stack gases.

28. Air Pollutant Properties

Project Leaders D. Garvin and R. F. Hampson, Physical Chemistry Division

Objective

Produce a compilation of data on the properties of air pollutants.

Approach

Employ the resources of the Data Centers of the Office of Standard Reference Data to evaluate and compile existing data on the properties of air pollutants.

Progress

A. Physical properties: A preliminary draft of the tables on physical properties was prepared during the summer of 1972. After reviewing this material it was decided to expand the coverage of properties and to enlist the aid of various experts at NBS and elsewhere in the compilation and evaluation of data. At the present time we have received contributions on electron affinities, dipole moments, polarizabilities, PVT properties, microwave spectra and isotopic composition of molecules. Other contributions are still being prepared.

B. Chemical Kinetics and Photochemistry: It is our plan to include in this compilation a set of tables of rate constants for chemical reactions, quantium yields for photolysis processes and optical absorption coefficients for pollutants and the normal constituents of air. Data have been evaluated

for reactions and photo processes in the $O_x/NO_x/HO_x/HNO_x$ system. Selections of rate constants for reactions of organic species still must be made.

The plan is to complete this work during FY 1974.

The following data evaluations were issued during the year. Direct distribution of reports is made to about 300 kineticists and atmospheric modellers. Data in these reports will be used in the proposed handbook.

1. R. F. Hampson, et. al. "Survey of Photochemical and Rate Data for Twenty-eight Reactions of Interest in Atmospheric Chemistry" J. Phys. Chem. Ref. Data 2 No. 2 (in press summer 1972). This article is a revision of the data sheets issued earlier as NBS Reports 10692 (Jan 1972) and 10828 (April 1972).

2. David Garvin, editor "Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions" NBSIR 73-206 (May 1973). These are data evaluations made for us by scientists not at NBS.

3. R. F. Hampson, et. al. "Chemical Kinetics Data Survey VI. Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Atmospheric Chemistry" NBSIR 73-207 (Summer 1973, now being reviewed).

29. Degradation of Polymers

Project Leader R. E. Florin, Polymer Division
Other Personnel L. Dunlap, W. J. Pummer, S. Straus, C. N. Cascaval (Guest worker) and Roestamsjah (Guest Worker)

Objective

The objective of this project is to gain as full an understanding as possible of the mechanisms of polymer degradations of all sorts. Special emphasis is placed on thermal degradation to volatiles. This is important in its application to limits on service conditions, to fire hazard, to incineration, and to production of toxic or irritating volatile products. Application of the knowledge to various situations, e.g., fires, is also involved.

Approach

Mechanism is most readily deduced from studies of pyrolysis in vacuum, the curves of rate and of molecular weight versus conversion to volatiles being the most important data. For new polymers, products are characterized by mass spectrometry, gas chromatography, and measurement of molecular weight, etc. Interpretation is in terms of the free radical chain theory, often quantitatively developed. The influence of inert gases and oxygen is is also being studied.

Progress

Data were acquired for rates of pyrolysis of polyimide as a function of film thickness and oxygen partial pressure.

Initial data of this sort were obtained for polystyrene. The reduction in decomposition temperatures in going to an air environment is of the order of 50 to 100°. Initial data were obtained for oxidative pyrolysis of polystyrene.

A comprehensive experimental and theoretical study of the pyrolysis in vacuum of polystyrene was completed and published. The initiation step is principally at chain ends with a minor random scission component for thermally prepared polystyrene. However, for an ionically prepared polystyrene, initiations is at first exclusively random scission. Supplementary work with azobis-isobutyronitrile prepared polystyrene was begun, and pyrolysis of polyalpha methylstyrene at molecular weights extending to 10 million. Pyrolysis studies of polyoctafluorostyrene were begun. Pyrolysis gas chromatography was used to survey decomposition products of many hydrofluoro copolymers and certain anomalous polystyrenes.

Burning behavior was studied in the limiting oxygen index apparatus for transition-metal containing ionomers (i.e., ethylene-methacrylic acid copolymers). The same equipment was used to study the modifications in burning behavior of polymers caused by gamma ray induced degradation and crosslinking. Oxygen index increases of a few points were sometimes found.

30. Low Velocity Measurements in Water Pollution

Project Leader G. Kulin, Mechanics Division

Objective

The objective of this project is to improve the state-of-the-art of measurement of low velocities of water as practiced in the field by instrument users concerned with water pollution abatement. For this purpose "low" velocity is defined as less than approximately 1 foot per second, but with emphasis on the lower end of the range, down to 0.1 fps and even lower. These low velocities play major roles in lake, reservoir and estuary dynamics and have attained increased importance because of recent intense interest in water quality control and marine disposal of thermal discharges and other wastes. The design specifications for the new NBS water tunnel now under construction anticipated this need and provided for test section velocities down to 0.1 fps.

Approach

The approach is two-pronged, consisting of a field contact program and a laboratory program.

Field Contacts: Special effort is being made to contact personally people who have the responsibility of making low-velocity measurements in the field. The purposes of the contact program are to:

·Observe field work firsthand and identify measurement problems met on site.

Survey present instrumentation capability and identify accuracies attained compared with accuracies required now or anticipated in the future.

Generally establish or improve communications with instrument users in the field.

The results of the field contacts program hopefully will help us to identify and plan purposeful experiments to supplement the NBS low-velocity measurements program and will foster transfer of NBS measurement capability where such improved transfer would be benefical in the field.

Laboratory Program: The laboratory program includes three phases, all of which are subject to adjustments by inputs from the field contact phase.

- Evaluation of present low-velocity measurement instruments including calibration methods, near-threshold performance, and error sources.
- Improvements on existing meters.
- Development and evaluation of new types of velocity measuring instruments.

Progress

During the year contacts were established with 60 organizations. Of these contacts, 16 were personal visits to field measurement sites and/or offices, and the remainder were mostly telephone communications with a few letter communications. The organizations contacted included 30 Government (federal, state and local) agencies, 19 private companies, 9 university laboratories and 2 trade associations. This is a continuing effort.

Some of the major preliminary conclusions, which will be described in more detail together with documentation

in a forthcoming internal report are as follows:

- Improvements in low-velocity measurements are needed. Commercially available instruments for measuring very low velocities are not doing the job under all conditions. Most of the problems are technological but some appear to be hydrodynamic in origin.
- Regulatory requirements have created a need for more low-velocity measurements for environmental impact statements, etc., but as yet there are no requirements on accuracy of specific velocity measurements.
- Many of these measurements are being performed by capable and experienced people who are specialists in this field. However, the extent to which this is not true is probably significant and is still under investigation.
- Velocity measurements for pollution abatement are intimately related to flowrate measurements for water delivery systems and industrial and municipal wastewater effluents. Improved velocity measurements are needed for velocity-area flowrate integarations and for in-place calibrations of wastewater meters.
- Field practice in wastewater measurements in small industries is often very poor and measurements are made by inexperienced personnel.
- Regulatory agencies need improved instruments and methods for monitoring industrial effluent flowrates.

In the laboratory an investigation was started on the low-velocity near-threshold performance of rotating-bucket vertical-axis current meters. This is being done in a small towing tank. Results to date suggest that the Price meter is a better low-velocity performer than it is generally given credit for.

The survey of field contacts will be continued in order

to fill gaps in the information, to delineate better areas where help is needed and to consider the most effective methods for transferring measurement capability where needed.

In the laboratory, the evaluation of rotating-bucket meters will be continued. Additional work during FY 74 will be selected from the following, subject to modification by field contact results and to availability of facilities.

- Evaluation of miniature propeller and other meters for field use and for suitability for flowrate meter field calibrations.
- Evaluation of towing tank test procedures for very low velocities and comparison with calibrations in the existing open-circuit water tunnel and the new high-performance tunnel (scheduled to come on line late in FY 1974).

31. Fate and Effects of Oil in the Seas

Project Leader S. Wasik, Physical Chemistry Division
Other Personnel G. T. Armstrong, R. L. Brown, and J. I. Minor, Jr.

Objective

Develop a method for indentifying and measuring the solubilities of individual components of oil-water and processed oil-water extracts.

Approach

A repetitive gas phase extraction technique is used followed by analysis of the gas phase in a gas-liquid chromatography column. The physical chemical studies may be divided into two parts: (1) the determination of solubilities and partition coefficients of hydrocarbons in sea water and (2) the development of analytical gas chromatography columns for the separation of hydrocarbons from their deuterated analogs.

Progress

A. Hydrocarbon solubility: A method for identifying and measuring the solubilities of the individual components of petroleum and processed oil-water extracts has been developed. A paper describing these results was presented at the 1973 Conference on Prevention and Control of Oil Spill meeting held in Washington, D. C. in March 1973. This aspect of the work is important in that it demonstrates the strong effect the higher alkanes (C_{12}-C_{22}) have on the solubility of the toxic aromatic hydrocarbons.

The higher alkanes form emulsions on shaking which are stable for long periods of time. The solubilities of the volatile aromatic hydrocarbons are enhanced by the presence of these emulsions.

The partition coefficients and solubilities of cyclohexane, cyclohexene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, and benzene have been measured in fresh and sea water over the temperature range 0-25°C. The results indicate that the partition coefficients and solubilities of hydrocarbons in aqueous solutions increase with the degree of unsaturation of the hydrocarbons.

A paper describing the results of solubility and partition coefficient measurements on dimethyl mercury in fresh and sea water is almost completed.

B. Analytical column development: To date, we have been able to separate the volatile aromatic (benzene, toluene, and the xylenes), the olefinic (ethylene, butene, and pentene) and the aliphatic hydrocarbons (n-octane) from their deuterated analogs. The first two separations were obtained using an aqueous silver nitrate column while the latter separation was achieved on a liquid crystal column. These columns should prove useful for isotope dilution analyses of trace amounts of hydrocarbons in sea water.

32. Transformations of Heavy Metals in Aquatic Environments

Project Leaders F. E. Brinckman, Inorganic Materials Division and W. P. Iverson, Metallurgy Division

Objective

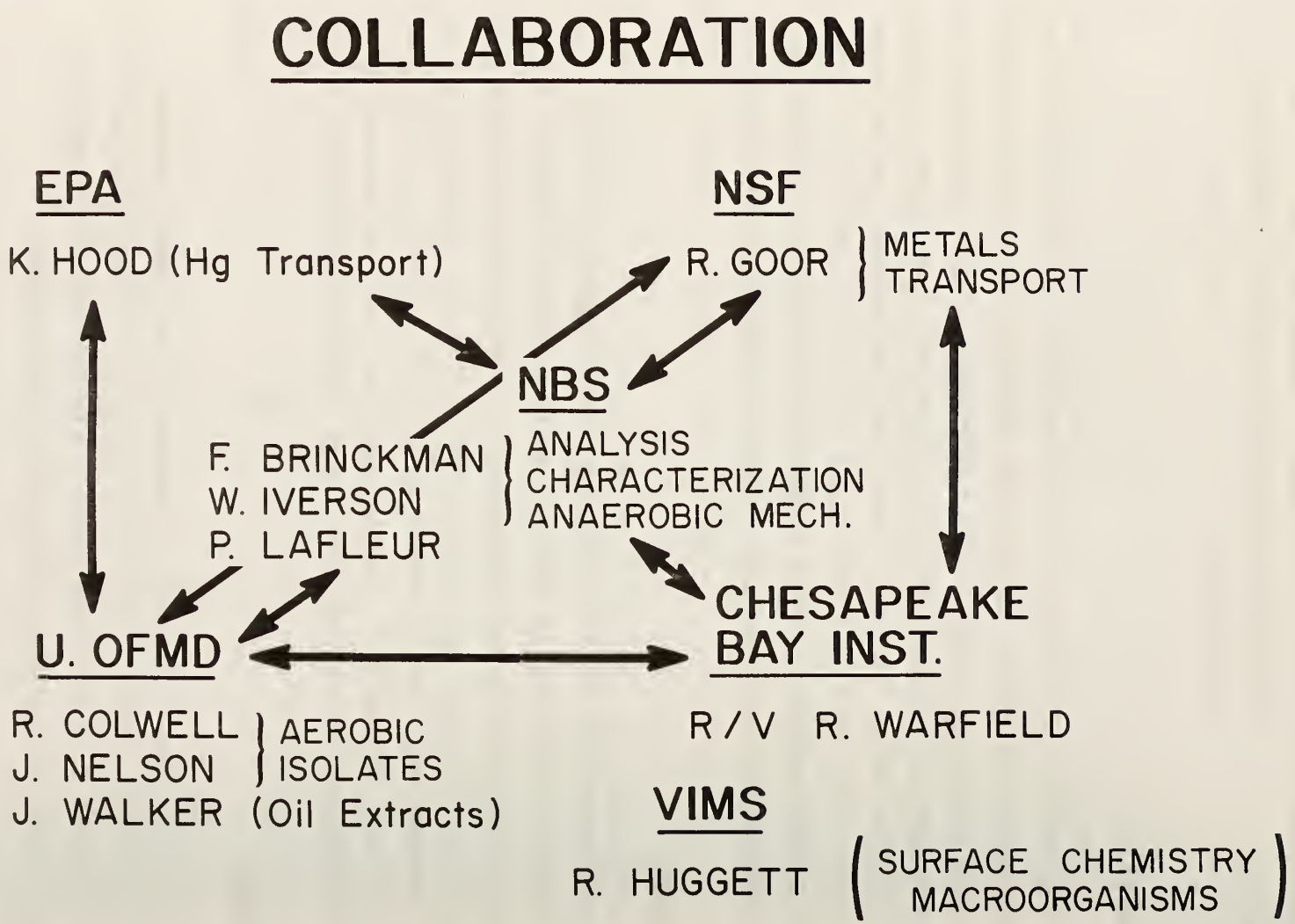
The principal objective of this project is to characterize biological and other mechanisms operative in natural water systems for mobilization and transport of heavy metals. It is expected that information derived from these studies can provide keys for the prevention or control of release of such heavy metals in the highly toxic forms (viz. methyl- and dimethylmercury) from already established reservoirs in natural bodies of water (rivers, estuaries, etc.).

Approach

An understanding of the chemical and biological nature of metals transport in natural waters necessitates a balanced interdisciplinary approach to characterizing key pathways. The NBS interdivisional team is comprised of an organometal chemist and a biologist expert in microbial corrosion. The effort has involved outside sponsorship and collaboration along the lines depicted in Figure 32.1.

Progress

During the report period, a number of sediment, water, and plankton samples obtained from the Chesapeake Bay with Dr. Colwell's group have been analyzed for total mercury using flameless atomic absorption techniques.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MACROORGANISMS

Figure 32.1

A number of mercury tolerant aerobic bacteria isolated from the Chesapeake Bay by Dr. Colwell's group have been screened for their ability to produce free mercury or volatile organomercurials from phenylmercuric acetate.

In parallel with the microbiological investigations, we have studied non-enzymatic mercury transformations, primarily organic group transfer reactions between mercury and other metals in aqueous solution. It has been found by a combination of proton nuclear magnetic resonance and laser-Raman spectrometry that trimethyllead cation undergoes demethylation reactions in water similar to those as observed earlier for trimethyltin cation, e.g., rapid methylation of mercuric ion to methylmercury cation.

Moreover, the process of methylating mercuric ion is sensitive to the presence of certain counterions; for example, excess cyanide and thiocyanate anions effectively inhibit the transmethylation process noted above.

The significance of these results is the demonstration that non-enzmatic reaction pathways can substantially affect concentrations of organomercury cations in the presence of inorganic- or organo-cations of other metals in aquatic environments.

Project activities to date have resulted in publication or presentation of several aspects of the work:

1. "Biodegradation of Phenylmercuric Acetate by Mercury Resistant Bacteria," J. D. Nelson, W. Balir, F. E. Brinckman, R. R. Colwell, and W. P. Iverson, Appl. Microbiol., 26, 321 (1973)

2. "Transmethylation of Heavy Metal Ions in Water," F. E. Brinckman and K. L. Jewett, 8th Middle Atlantic Regional Mtg. of the Amer. Chem. Soc., Washington, D. C. January 1973, Abstracts of Papers, p.52.

33. Reactor Effluent and Environmental Radioactivity Standards

Project Leader W. B. Mann, Applied Radiation Division
Other Personnel B. M. Coursey, J. M. R. Hutchinson, J. R. Noyce

Objective

The objective is to improve the accuracy of measurements of radioactivity in the environment and in the effluents from nuclear facilities. In order to accomplish this, an immediate goal is to make all such measurements in the United States either directly or indirectly traceable to the National Bureau of Standards.

Approach

There are three major elements in our current approach to these objectives. (1) Traceability: We are working toward establishing traceability of radioactivity measurements of the major quality control laboratories with NBS. (2) Standard Reference Materials (SRM's): We are providing standard sources and test sources through the SRM program for general use by the nuclear industry and environmental monitoring laboratories. (3) Reference Laboratory: We are developing the capability to serve as a "third party" or referee laboratory to help resolve discrepancies involving environmental measurements of radioactivity.

Progress

Traceability

Over the past two years, we have engaged in a traceability

study with one of the national quality control laboratories. In connection with this study we have:

a. provided the laboratory with 6 calibration standards,
b. provided 19 test sources and evaluated the laboratory's results for these sources,
c. sent the project leader to their laboratory to evaluate their instrumentation and methods of analysis, and
d. provided them a calibrated mixture which they then distributed as an unknown to laboratories under their jurisdiction, such as the state radiological health laboratories.

This mixture (d) closely simulated a reactor waste water sample, as it contained the beta-particle emitters hydrogen-3 and strontium-90, as well as three gamma-ray-emitting radionuclides.

Standard Reference Materials

The following sources, which are useful for calibrating instruments used in environmental radioactivity measurements, have been distributed by this section during the past two years.

a. Mixed Radionuclide Gamma-Ray Emission-Rate SRM's: The composition of the four mixtures prepared to date is given in Table 33.1.
b. Iodine-131: A special distribution of solution standards of iodine-131 was made to 23 laboratories.
c. Iodine-129 (SRM4949): Solution standards of iodine-129 were prepared. (This work was <u>not</u> supported by the AEC contract.)

During the past two years we have worked to improve our low-level radioactivity measurements capabilities by:

a. improving our apparatus (A list of major counting systems developed for this laboratory is given in Table 33.2.)
b. developing our expertise in low-level radiochemistry techniques, and
c. engaging in intercomparison studies.

A specific example of the latter two items was our participation in an international intercomparison, sponsored by the IAEA, Monaco (2). Twenty-four of the participants determined the strontium-90 content of lyopholized, homogenized seaweed. The values reported ranged from 2.4 to 15.6 pCi/g. The average value, excluding the outlying lowest value, was 10.0 pCi/g. The NBS value was 10.1 pCi/g.

Future Plans

Traceability: We will continue and expand traceability studies with major quality control laboratories, and extend these studies to include the state laboratories.

SRM Program: The mixed radionuclide SRM's will be reissued at least annually. Strontium-90 and strontium-89 solution standards will be distributed soon. A calibrated mixture of the two will also be made available.

Reference Laboratory: River sediment samples, with environmental levels of radioactivity, are being developed. Liquid scintillation counting techniques are being developed

for low-level measurements of hydrogen-3 and selected alpha-particle emitters in environmental water samples, A new anticoincidence shielded Ge(Li) detector system will be used to assay environmental samples.

Table 33.1. NBS Mixed Radionuclide Gamma-Ray Emission-Rate Standards and Test Sources

(A) List of standards and test sources

SRM No.	Description	Prepared From Master Solution No.[a]
Test source[b]	450-ml solution	I
Test source[b]	50-ml solution	I
4242-B	450-ml solution	II
4243-B	50-ml solution	II
4244-B	15-ml solution	II
4252[c]	450-ml solution	III
4253[c]	50-ml solution	III
4242-C	450-ml solution	IV
4243-C	50-ml solution	IV
4215	point source	IV
4216	point source	IV

a. Four master radionuclide solutions have been prepared. Sources in several different forms are normally prepared from the same master solution.

b. These two sources were distributed as unknowns in a "round robin" intorcomparison (1).

c. SRM-4252 and -4253 were first distributed as unknowns, An SRM certificate was later furnished to each user.

(B) Radionuclidic components in the four master solutions.

I	II	III	IV
^{51}Cr	^{54}Mn	^{51}Cr	^{57}Co
^{54}Mn	^{57}Co	^{54}Mn	^{60}Co
^{58}Co	^{60}Co	^{58}Co	^{85}Sr
^{59}Fe	^{88}Y	^{59}Fe	^{88}Y
^{65}Zn	^{109}Cd	^{60}Co	^{109}Cd
^{137}Cs-^{137m}Ba	^{113}Sn-^{113m}In	^{65}Zn	^{113}Sn-^{113m}In
	^{137}Cs-^{137m}Ba	^{134}Cs	^{137}Cs-^{137m}Ba
		^{137}Cs-^{137m}Ba	^{139}Ce
		^{144}Ce-^{144}Pr	^{203}Hg

Table 33.2- Major Counting Systems for Reference Laboratory[a]

For the analysis of gamma-ray emitters:

(1) Anticoincidence shielded Ge(Li) detector system
(2) 8" x 4" - "$4\pi\gamma$" - NaI(Tl) scintillation detector system
(3) 5" dia. - NaI(Tl) scintillation well detector system

The above systems are used in conjunction with two Northern Scientific MCA's of 1024 and 4096 channel

For the analysis of beta-particle emitters:

(1) Omniguard gas-flow proportional counter
(2) Sharp low-beta counting system
(3) Packard 3320 liquid scintillation counter

For the analysis of alpha-particle emitters:

(1) silicon surface barrier detectors
(2) liquid scintillation counter

The Northern Scientific MCA's may be used with these two methods.

(3) HASL "b-raters"

[a]The use of a particular manufactured product does not constitute an endorsement of the product by the National Bureau of Standards.

34. Noble Gas Radionuclides

Project Leader W. B. Mann, Applied Radiation Division
Other Personnel F. J. Schima, M. P. Unterweger

Objective

The objective of this program is to improve the detection and measurement capabilities for noble gas fission products by means of the preparation of activity calibrated samples of various gaseous radionuclides. Further, production mechanisms and decay characteristics of these radionuclides will be studied insofar as they might be relevant.

Approach

The gaseous radionuclides are generally calibrated in activity/ gram mole units by means of length compensated gas proportional counters. These counters are operated very close to 100% efficiency for decay event detection. A portion of the gas radionuclide sample is then diluted to the desired activity level in a gas handling system which contains very accurate barometers and measured volume chambers. In the related work, the general facilities of the Radioactivity Section as well as the Center for Radiation Research are made use of as needed. For example, the isotope separator is used to prepare samples of ^{133}Xe free from ^{131m}Xe.

Progress

Table 34.1 is a list of the gaseous radionuclide samples which have been prepared in the last year with some as Standard Reference Material. Due to short half-lives ^{133}Xe

appears in the list (Table 34.2) of environmental related organizations which have obtained some of these samples. The ^{131m}Xe and ^{133}Xe radionuclides have medical applications, but without significant environmental impact.

Additional work includes the measurement of ^{133}Xe and ^{135}Xe production cross-section by the $(n_{th}, \alpha)a)$ reactions on Ba isotopes.

These results are:

for $^{138}Ba(n_{th}, \alpha)^{135}Xe$ $\sigma < 21 \mu b$;

for $^{136}Ba(n_{th}, \alpha)^{133}Xe$ $\sigma \lesssim 50 \pm 20 \mu b$.

The 8.89±.02d half-life measurement for ^{129}mXe radionuclide was published in the last year.

References

1. L. D. Miller and F. J. Schima "The Half-Life of ^{129m}Xe", Int. J. Appl. Rad. Isotopes, 24, 353 (1973).

2. S. B. Garfinkel, W. B. Mann, F. J. Schima and M. P. Unterweger "Present Status in the Field of Internal Gas Counting" Nuel. Instr. & Methods (in press).

Future Plans

It is planned to gas count several of the ^{85}Kr samples, in order to determine an activity value with accuracy sufficient for OSRM certification. Related to the current ^{133}Xe calibration, ssamples will sent directly to seven state laboratories, under the AEC program for delegating to the States responsibility for environmental monitoring of reactor effluents.

Table 34.1

Gas Radionuclides

Nuclide	Nominal Activity (dpm/ml)	OSRM # If applicable
^{14}C	in process	
^{37}Ar	11,000	4300
^{37}Ar	10	4301
^{85}Kr	100	--
^{131m}Xe	15,000	4305
^{133}Xe	15,000	--
^{133}Xe	in process	

Table 34.2

Gaseous Radionuclide Sample Users

A.E.C.	Division of Compliance, HSL	Idaho
A.E.C.	Nuclear Division, ORNL	Oak Ridge, Tenn
E.P.A.	Western Environmental Research Laboratory	Nevada
N.B.S.	Analytical Chemistry, IMR	
Smithsonian Institute - Astrophysical Obs.		Massachusetts

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14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

This report is a project-by-project description of the Measures for Air Quality program covering the fiscal years 1972 and 1973. Participation in the program is bureau-wide but the program office operates out of the Institute for Materials Research. Although air pollution measurement science has formed the major thrust of the program, it has been extended in FY 73 to include the beginnings of a water pollution effort to respond to new needs, particularly those arising out of the requirements of the Federal Water Pollution Control Act of 1972. A report on the MAQ program for FY 72 was not issued. However, the project reports in the current document include progress made during FY 72 for those FY 73 projects which were active in FY 72. Where a project was terminated at the end of FY 72 its description is included in the present document with appropriate notation.

In water pollution the situation is much more complex since there are many more pollutants in more types of water that will be subject to control under the Federal Water Pollution Control of 1972. When a pollutant is of concern in the discharge permit program, water quality standards, the toxic pollutant list and in the specimen bank program, the state of the measurement art is scrutinized at NBS and the need for development assessed.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Air pollution; measurement; Standard Reference Material; water pollution.

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